Refining Synthetic Liquids from Coal and Shale

Energy Engineering Board
Assembly of Engineering

Carnegie-Mellon University
PITTSBURGH PENNSYLVANIA 1900

Refining Synthetic Liquids from Coal and Shale

Final Report
of the
Panel on R&D Needs in
Refining of Coal and Shale Liquids

Energy Engineering Board
Assembly of Engineering

NATIONAL ACADEMY PRESS
Washington, D.C. 1980

This report has been reviewed by a group other than the author
according to procedures approved by a Report Review Committee con
of members of the National Academy of Sciences, the National Acad
of Engineering, and the Institute of Medicine.

The National Research Council was established by the National Aca
of Sciences in 1916 to associate the broad community of science a
technology with the Academy's purposes of furthering knowledge an
advising the federal government. The Council operates in accorda
with general policies determined by the Academy under the authori
of its Congressional charter of 1863, which establishes the Acade
a private, non-profit, self-governing membership corporation. Th
Council has become the principal operating agency of both the Aca
of Sciences and the National Academy of Engineering in the conduc
their services to the government, the public, and the scientific
engineering communities. It is administered jointly by both Acad
and the Institute of Medicine. The Academy of Engineering and th
Institute of Medicine were established in 1964 and 1970, respecti
under the charter of the Academy of Sciences.

The study culminating with this report was performed under contra
number E(49-18)-1216 between the U.S. Energy Research and Develop
Administration and the National Academy of Sciences.

Library of Congress Catalog Card No. 80-84515

International Standard Book Number 0-309-03129-X

Available from

NATIONAL ACADEMY PRESS
2101 Constitution Avenue, N.W.
Washington, D.C. 20418

Printed in the United States of America

PREFACE

During the 1980s, additions to world petroleum reserves are expected to continue to fall behind production. In this situation, these dwindling reserves will no longer be adequate as the only source of liquid fuels.

Although steps are being taken to supplement the supply of energy from petroleum with energy from a variety of other sources, the need for alternate supplies of liquid fuels for passenger and freight transportation is particularly urgent. The most promising sources for the large quantities of liquid fuels required by the United States are, at present, the ample supplies of coal and oil shale in this country, but the technology for producing and using these synthetic fuels needs to be advanced before full-scale facilities can be constructed and brought on stream. Especially important is a better understanding of the health and environmental impacts of synthetic fuel production and use, and of the means for bringing these impacts down to acceptably low levels.

The National Research Council began to study the problems of converting coal into liquid fuels in 1975, under a contract from the U.S. Energy Research and Development Administration (ERDA, subsequently incorporated into the Department of Energy). On the completion of this study in 1977,[a] ERDA contracted for a follow-on study of the R&D needed for the refining of coal and shale liquids. The results of this study are contained in this report.

In this follow-on study, the National Research Council was asked to undertake the following tasks:

- Survey the state-of-the-art of programs currently underway on the application of petroleum processing techniques to the upgrading of coal and shale liquids.

---

[a]The study, titled "Assessment of Technology for the Liquefaction of Coal," was carried out by the Ad Hoc Panel on Liquefaction of Coal,

cost standpoint.

- Recommend a course of direction for the achievement of short and long term goals.

In the contract, ERDA also specified the following:

- The primary emphasis of the study should be placed on fuel production, with the production of chemical feedstocks examined only where they may be appropriate by-products in the normal operation of a commercial coal or shale oil refinery.

- Attention should be given to the types of fuel that will be needed after 1985, when synfuel plants are expected to be operating.

- Priorities in the recommended research programs should be clearly described and rationalized with respect to appropriate technical and economic criteria.

Evaluating the processing techniques used in upgrading coal and shale liquids has been the equivalent of shooting at a moving target. When the study began, for example, it was expected that an important use for the liquids would be as boiler fuels. However, as methods for the more complete conversion of coal to distillable fuels were demonstrated, they became the preferred means of removing ash and were incorporated in three of the four plants for demonstrating coal conversion. This report covers both types of liquids, but with emphasis on the distillable synthetic liquids.

This panel did not assess refining costs in detail. Costs of refining synthetic fuels should not differ greatly from conventional petroleum refining. The major cost uncertainties are in the initial conversion steps, not in the refining process.

The study, consistent with its charge, concentrated on the refining of distillable liquids produced by direct liquefaction processes. The panel believes that indirect liquefaction, while potentially important, presents few difficult research and development problems, given its long history and major industry involvement.

AD HOC PANEL ON R&D NEEDS IN REFINING OF COAL AND SHALE LIQUIDS

ARTHUR L. CONN (Chairman), Arthur L. Conn & Associates, Ltd., Chicago

DAVID L. COFFIN, U.S. Environmental Protection Agency, Health Effects Research Laboratory, Research Triangle Park, North Carolina

JOSEPH L. COLUCCI, General Motors Research Laboratories, Warren, Michigan

MELBOURNE G. FRYBACK, Synthetic Fuels Department, Sunoco Energy Development Company, Dallas, Texas

JAMES R. KATZER, Department of Chemical Engineering, University of Delaware, Newark, Delaware

JOHN P. LONGWELL, Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts

C. DWIGHT PRATER, Mobil Research and Development, Paulsboro, New Jersey

MORGAN C. SZE, The Lummus Company, Bloomfield, New Jersey

ROY F. WESTON, Roy F. Weston, Inc., West Chester, Pennsylvania

---

JOHN O. BERGA, Study Director

DUNCAN M. BROWN, Staff Officer
RITA M. BYRNES, Editor

JOHN A. PHINNEY, Consultant

ENERGY ENGINEERING BOARD

ROBERT H. CANNON, Jr., (Chairman), Stanford University, Department of Aeronautics and Astronautics

FLOYD L. CULLER, JR., Electric Power Research Institute

W. KENNETH DAVIS, Bechtel Power Corporation

R. EUGENE GOODSON, Purdue University, Institute for Interdisciplinary Engineering Studies

EDWARD J. GORNOWSKI, Exxon Research and Engineering Company

WILLIAM R. GOULD, Southern California Edison Company

LESTER B. LAVE, The Brookings Institution

JOHN P. LONGWELL, Massachusetts Institute of Technology, Department of Chemical Engineering

ERIC H. REICHL, Consultant

WILLIAM C. REYNOLDS, Stanford University, Department of Mechanical Engineering

RONALD SMELT, Lockheed Aircraft Corporation (retired)

JOHN O. BERGA, Executive Director

CONTENTS

1 SUMMARY 1
Future Product Requirements 1
Liquefaction Processes 2
Refining Technology 4
Hydrogen Manufacture 5
Health and Environmental Problems 6
Recommendations for Research and Development 7

2 INTRODUCTION 9
Projection of the Petroleum Supply 10
Maximizing Efficiencies 10
Liquid Fuels from Oil Shale and Coal 14
Bibliography 15

3 FUTURE PRODUCT REQUIREMENTS 17
Utilization of Liquid Fuels 18
Electric Power Generation 18
The Industrial Sector 18
The Buildings Sector 18
Nonenergy Uses 18
The Transportation Sector 19
Types of Liquid Fuels Required 21
Heavy Fuel Oils 21
Mid-Distillates 22
Gasoline 22
Future Transportation Fuels 25
Gasoline 25
Diesel Fuel 26
Aviation Fuel 26
Future Automotive Engines and their Fuel Needs 29
Homogeneous-Charge Spark-Ignition Engine (Carbureted) 29
Homogeneous-Charge Stratified-Charge Engine (Timed Fuel Injection) 30

Engines 35
Survey on Compatibility of Future Automotive Fuels and Engines 35
Summary of Responses 39
Bibliography 44

4 COAL LIQUEFACTION PROCESSES 46
The Role of Hydrogen 46
Coal Pyrolysis 48
Solvent Processes Without the Addition of Catalysts 52
Solvent Processes Involving the Addition of Catalysts 57
Exxon Donor Solvent (EDS) Process 58
H-Coal Process 61
Hydrogen Production and Use in Direct Liquefaction Processes 63
Direct Liquefaction Processs with Decreased Hydrogen Consumption 66
Indirect Liquefaction Processes 66
Bibliography 75

5 OIL SHALE EXTRACTION PROCESSES AND PRODUCTS 78
Surface Retorting Processes 79
Lurgi-Ruhrgas Process 79
Superior's Multi-Mineral Process 81
Paraho Process 81
Tosco II Process 84
Union Oil Retorting Processes 86
In Situ Retorting Processes 88
Occidental Petroleum Process 88
LETC Process 89
Lawrence Livermore Laboratory's RISE Process 94
Physical and Chemical Data on Raw Shale Oil from Various Retorting Processes 94
Nitrogen 102
Arsenic 105
Sulfur 108
Oxygen 108
Bibliography 108

Direct Liquefaction 117
Indirectly Produced Coal-Derived Liquids 118
Refining Shale Liquids 118
Refining Technology for Catalytic Hydroprocessing 125
Overview 125
Catalysts 127
Reactors and Processes 130
Conclusions 133
Recommendations 134
Bibliography 135

7 HYDROGEN PRODUCTION 137
Production Processes 137
Steam Reforming 137
Partial Oxidation 138
Hydrogen from Coal 139
Other Processes 140
Comparative Costs 140
Conclusions and Recommendations 143
Bibliography 145

8 ENVIRONMENTAL EFFECTS 146
Location of the Refining Operation 147
Chemical Composition of Synthetic Crudes 147
Heteroatoms 148
Polycyclic Organic Materials (POMs) 149
Trace Elements 150
Regulations and Constraints 151
Control Technologies 153
Public Concerns 154
Recommendations 155
Bibliography 155

9 HEALTH EFFECTS 159
Health Effects of Petroleum Refining and Handling 159
Occupational Studies 161
Shale Oil Refining and Handling 163
Scottish Studies 163
Estonian Studies 164
U.S. Studies 165
Coal Oil Refining and Handling 169

Gasoline 172
Mid-Distillates 172
Residual Fuels 173
Combustion Particles 173
Conclusions and Recommendations 173
Bibliography 174

10 RESEARCH AND DEVELOPMENT 183
Federally Funded R&D 184
Department of Energy In-House Refining R&D Capability 185
Privately Funded R&D 187
R&D Priorities 189
Future Product Requirements 189
Catalyst Development 190
Disposal of Arsenic Wastes from Shale Oil Refining 190
Hydrogen Production 190
Chemistry of Raw Liquids and Chemical Reactons in Refining 191
Indirect Liquefaction 191
Health and Environmental Impacts 191
Recommendations 192
Basic and Exploratory Research 192
Applied Research and Process Development 193
Systems Development 194
Bibliography 194
Appendix 195

1 SUMMARY

The purpose of this study was to determine the status of research and of technology for refining liquids from oil shale or coal, to recommend areas for future research and development emphasis, and to make recommendations on the roles of government and industry in these areas.

Refining is the link between the primary production of liquids from these solid hydrocarbon sources and the supply of liquid fuels meeting the requirements of the various consumers. But use patterns and combustion equipment are expected to change with time, and the compositions of liquids produced by the variety of raw materials and conversion processes, which differ from those associated with petroleum, will also probably change with time. Therefore, parts of this report are devoted to discussions of liquefaction technologies and the corresponding liquid compositions, the committee's view of coming changes in demand for various types of liquid fuels, and the possibilities for evolution in end-use equipment.

Today's refining technology for these synthetic liquids adds hydrogen to eliminate elements other than carbon and hydrogen and thus produce substances similar to petroleum hydrocarbons. Because the manufacture and use of hydrogen are the major sources of energy consumption and expense in refining these liquids, the technology and research needs for hydrogen manufacture are also considered in this study. Environmental and health problems are given careful attention since the raw liquids are known to contain toxic components.

FUTURE PRODUCT REQUIREMENTS

The major categories of liquid fuels are gasoline, which distills at temperatures below approximately 430°F; middle distillates (kerosene, diesel fuel, and domestic heating oil) which distill below 700°F, and fuel oils which distill above 700°F. Fuel oils are used in electric power generation, industrial heating, and some smaller commercial installations. Because of limitations of natural gas supply, the

combustion and handling techniques for dealing with the high nitrogen content, and (in the case of coal liquids) the relatively high content of skin carcinogens, will be required. For smaller installations such as apartment houses and small factories, it is probable that more refined grades will be required.

During this century gasoline consumption is not expected to grow and may decrease as prices increase and more fuel efficient passenger automobiles displace the present fleet. While future use of fuel injection, stratified charge engines, or engines with higher compression ratios may call for adjustments in volatility and aromatic content, it is believed that these requirements can be easily met by applying petroleum refining technology to the lower boiling fractions produced from coal and oil shale once nitrogen, sulfur, and oxygen have been removed. Because of their high aromatic content, these fractions are especially well suited for this use.

The projected increase in use of diesel engines, increased air travel, and continued use of liquid fuels for home heating should result in a considerable increase in middle distillate demand relative to that for gasoline. A high hydrogen content is needed in these fuels to avoid smoke and deposit formation in present equipment and, in the case of the diesel engine, to give satisfactory ignition characteristics. Coal liquids from direct liquefaction processes, because of their low hydrogen content, are at a disadvantage compared with shale oil, which has relatively high hydrogen contents, or with indirect liquefaction products, which normally have very high hydrogen content. Automotive gas turbine, Stirling, or stratified-charge engines, which can tolerate lower hydrogen contents, are not expected to be used widely before the end of this century.

In the long term it is expected that the fraction of total liquid fuel production used in transportation will increase substantially from its present share of approximately 50 percent.

LIQUEFACTION PROCESSES

The two major categories of liquefaction processes are "direct" and "indirect." Direct liquefaction processes involve heating the solid starting material with or without the presence of catalysts, hydrogen, or solvents. Varying fractions of the organic content are converted to liquids and can subsequently be separated from the unconverted solids. Indirect liquefaction refers to a class of processes in which the solid organic material is first converted to a mixture of carbon monoxide and hydrogen by reaction with oxygen and/or steam. After purification, this

the gasoline or distillate boiling range. It is anticipated that both classes of processes will see considerable application in the future, with the choice depending on the nature of the raw materials available, the types of products required, and the technological maturity of particular processes. While the liquids produced by indirect liquefaction will require further purification and refining, major problems are not foreseen. This study, therefore, concentrates on the refining problems involved in converting liquids from direct liquefaction processes to acceptable products.

Heating without adding hydrogen or solvents is called pyrolysis. With the western oil shales, high recoveries of the organic fraction can be achieved by pyrolysis, and a variety of retorts have been proposed for this purpose. There is also considerable interest in in situ retorting, in which most of the operation is carried out underground. The shale is explosively fragmented, and a flame is propagated downward through the broken stone by pumping air downward. The heat from this flame drives off pyrolysis products, which run to the bottom of the fractured zone, and the flame is fed by the char that remains in the stone. The oil produced is more volatile than that obtained in above-ground retorting, probably due to a higher level of thermal conversion. However, its properties are otherwise quite similar to those of shale oil retorted above ground and do not present significantly different refining problems.

Pyrolysis has also been used in the liquefaction of coal, but the processes developed thus far yield relatively small amounts of liquids (usually less than 30 percent of the coal feed), accompanied by large quantities of char that can be disposed of as a boiler fuel. The liquid is in the form of a very heavy tar that can be used as a low grade liquid fuel or refined to a higher grade fuel.

Higher yields of liquids are obtained by the use of liquid phase processes in which most of the coal is dissolved in a coal-derived recycle liquid which also supplies hydrogen "donors" to upgrade the hydrocarbons in the coal. In general, the recycle liquid is catalytically rehydrogenated either in an external circuit (as in the Exxon Donor Solvent, or EDS, process) or in the presence of the coal and ash (as in the H-Coal and Solvent-Refined Coal II, or SRC-II, processes).

The properties of the liquids obtained depend, of course, on the coal used. They also depend strongly on the amount of hydrogen added during liquefaction. Processes such as SRC-I, which add a minimal amount of hydrogen, produce a relatively high molecular weight tar. A process such as EDS, which consumes a large quantity of hydrogen, can produce a product more than 25 percent of which is in the gasoline boiling range.

In all cases, however, these liquids contain unacceptable amounts of nitrogen, oxygen, and polynuclear aromatics, and require further purification.

REFINING TECHNOLOGY

Today's refining technology has been highly optimized for the conversion of a wide variety of petroleum crudes to meet the consumer's fuel requirements. The United States has maintained technological leadership in this field, and American processes are used in the bulk of the world's refining installations. These processes reduce to acceptable values the nitrogen, oxygen, sulfur, polynuclear aromatics, and metals such as vanadium, iron, and nickel originally present in the crude oil. However, the nitrogen, oxygen, and polynuclear aromatic contents of shale- and coal-based liquids are generally higher than those of petroleum crudes, and special process units will be needed to eliminate these undesirable components.

Hydrogenation is the basic technique for dealing with these materials, since by adding sufficient hydrogen all the organic components can be reduced to saturated hydrocarbons and the metals eliminated from the liquid products. Pilot plant studies of several hydrotreating processes have demonstrated the ability to produce satisfactory products from shale and coal liquids. These processes are primarily extensions of the catalytic processes developed for the desulfurization and denitrogenation of petroleum. With some further development, these processes could be used to refine shale and coal liquids, but they require large amounts of hydrogen, higher pressures, and lower feed rates, all of which entail extra expense. More hydrogen is consumed than is stoichiometrically needed for heteroatom removal, methane is produced as a by-product, and a higher level of aromatic saturation occurs. If higher selectivity can be achieved, substantial savings in the energy and expense required for hydrogen manufacture are, in principle, available. A substantial R&D program aimed at reduction of hydrogen consumption is clearly justified. Special emphasis on a search for chemical techniques other than extensions of the conventional catalytic hydrogenation is also needed.

The inorganic contents of synthetic oils vary widely. Those from processes involving distillation contain relatively little, while those produced by filtration or solvent precipitation can contain fairly large amounts. These inorganic materials can cause catalyst deactivation and plugging. Thus, more efficient processes for their removal prior to further catalytic treatment are needed.

Raw shale oil and some coal liquids are too viscous at ambient temperatures to be transported in unheated pipelines. In some cases, vis-

The optimum degree of refining at the liquefaction site will depend largely on the particular materials to be handled. In many cases, it may be desirable to refine the liquids to the point at which they can be accepted by conventional petroleum refineries. There are a number of reasons why integrating these new raw materials into the existing large refineries should prove to be an economically optimal route. First, future limitations on total liquid fuel supply will very likely result in some large refineries running at lower total capacity. Second, the refining of coal and shale liquids along with conventional petroleum may well present special opportunities for optimization in the manufacture of products.

A survey of industrial and government laboratory capabilities for carrying out R&D on the refining of coal and shale liquids shows that considerable work is in progress in this area. Responses from 29 companies indicate that more than 2000 persons are engaged in refining and product R&D in industry. About 10-20 percent of this effort is devoted to the refining of coal and shale liquids; however, the personnel and skills involved in petroleum-related process research can be easily transferred to the special problems of coal and shale liquids. Capabilities for applied research and process development are quite limited in governmental laboratories. Considerable relevant basic research is being carried out in industrial laboratories, but the need for new approaches to refining coal and shale liquids calls for an augmented basic research effort.

An increased effort is also needed to define the optimum product composition, taking into account future advances in combustion equipment as well as advances in refining technology. This effort would logically involve fuel manufacturers, engine and equipment manufacturers, and government supported research. Such a program has begun for commercial jet aircraft, but more needs to be done in other areas.

HYDROGEN MANUFACTURE

At present, most refineries do not require hydrogen manufacturing, since by-product hydrogen from gasoline manufacturing is adequate to meet petroleum hydrotreating needs. Large scale introduction of raw synthetic fuels would require manufactured hydrogen, as would most coal liquefaction processes. Hydrocarbon gases are currently the most economic and efficient raw material for hydrogen manufacture, but conservation of this valuable resource will require the use of coal as a starting point for hydrogen manufacture. Using coal as a feedstock is less expensive than producing hydrogen by electrolysis or by current exploratory thermal techniques. While the need for more hydrogen in the refining of synthetic liquids is likely to lead to slightly greater CO_2 generation than in petroleum re-

optimizing and developing processes that are further down the road (e.g., air oxidation in multiple-fluidized-bed systems or the use of CO_2 acceptors such as CaO or oxygen acceptors such as Fe).

HEALTH AND ENVIRONMENTAL PROBLEMS

The health and environmental problems posed by the refining of coal- and shale-based liquids and by their use by the consumer must be given careful study. Of greatest importance is the known ability of coal tars to cause skin cancers and possibly other cancers. This toxicity is due to the relatively high content of high-boiling polynuclear aromatic and heterocyclic compounds. Shale oil and petroleum contain less of these substances; however, severe thermal treatment greatly increases their concentrations, and certain heavy fuel oils produced by severe cracking are sufficiently active that special handling is currently required in their refining and use.

While there is considerable experience in the petroleum industry with handling such hazardous materials, introduction of coal- and shale-based liquids will require special attention to potential health problems and to obtaining, through research, a detailed understanding of the hazards posed by carcinogens, co-carcinogens, and mutagens in such liquids. Refining techniques must be capable of reducing this toxicity to an acceptable level. Fortunately, hydrogenation appears capable of converting the toxic materials in these oils to nontoxic hydrocarbons of higher hydrogen content. A survey of research and development on shale and coal liquids in industry and in the national laboratories shows that considerable work is being carried out in anticipation of the need for handling techniques for these materials. Research related to this problem should obviously have a high priority.

In the lower boiling range, the main health hazards have been identified as the toxicity of single-ring aromatics (particularly benzene) and the toxicity, on ingestion, of products such as gasoline and kerosene. These hazards are essentially identical to those associated with today's petroleum-based fuels.

Some raw shale oils have been found to contain amounts of arsenic sufficient to require removal before further processing or use. Handling and disposal of this arsenic is a relatively new refining problem that will require careful attention to avoid exposure during refining and long term environmental risk on disposal.

Refining coal and shale liquids will produce by-products such as ammonia, phenols, and sulfur compounds. These materials are encountered

and gas streams is available. However, capacities and efficiencies might require improvement because of the higher nitrogen and oxygen contents of shale- and coal-based liquids.

RECOMMENDATIONS FOR RESEARCH AND DEVELOPMENT

1. More government support should be given to fundamental research on the basic chemistry of refining shale and coal liquids. The potential for carrying out the necessary research exists in the laboratories of industry, the universities, and the Department of Energy, but it needs to be funded at a higher level.

2. Research in the environmental and health areas should be given high priority. The following problems are especially important:

   (a) Establishment of limits on the carcinogen contents of the various classes of fuels.

   (b) Establishment of appropriate handling procedures for the more toxic unrefined materials.

3. Since the capabilities for applied research and development (as distinguished from basic research) are much stronger in industry than in government and university laboratories, major Department of Energy participation in this aspect of the effort is not indicated. The Department should continue to sponsor tests of processes developed by industry, however, as a way of assessing the state of the technology.

4. A reduction in the total cost of refining shale and coal liquids should be a principal R&D objective. The hydrogen required to remove sulfur and nitrogen from these liquids and reduce their boiling points is responsible for a major part of this cost. The R&D necessary to improve the technology for producing hydrogen from coal and coal char should be sponsored by the Department of Energy.

5. R&D aimed at establishing the optimum combination of fuel composition and end-use equipment should be given high priority by government agencies. Full cooperation among government, the fuel industries, and the equipment manufacturing industries is essential.

6. Basic and applied research relevant to the following refining needs is of high priority:

   (a) New methods for removal of nitrogen, oxygen, and sulfur from coal and shale liquids. Selective removal of oxygen and nitrogen is particularly important.

removal.

(d) New methods for manufacture of hydrogen.

(e) The mechanism of deactivation of the catalysts used in removing nitrogen, oxygen, and sulfur. This will enable the development of longer-lived catalysts.

(f) Mechanisms of the viscosity and solubility changes that occur during storage of coal and shale liquids, and additives to improve stability.

7. Facilities are needed for the experimental refining of synthetic fuels in quantities sufficient for large scale testing.

2 INTRODUCTION

It is likely that synthetic fuels will begin to supplement petroleum-derived fuels in the next few years. This report considers the effects on refining requirements of introducing fuels derived from oil shale and coal. When the production and use of coal and shale derivatives get underway on a commercial scale, we shall begin to see many changes in products and end-use equipment.

An examination of the problem involved in the introduction of fuels derived from coal and shale requires, at the start, an estimate of the type and quantity of liquid fuels that are going to be required in the future. This calls for:

- A projection of the petroleum supply
- A projection of the trends in liquid fuel end use
- A projection of the way fuel composition requirements are likely to change over the years with changes in end-use technology, changes in fuel sources, and changes in refining technology.

The projections that were made in this study were based on the following premises:

- The total supply of liquid fuels will become increasingly limited and expensive with time.
- There will be substantial incentives to substitute other energy sources for liquid hydrocarbon fuels where economically and technically feasible, and consequently important shifts may occur in the types of liquid fuel used.
- Control of health-related emissions will result in an increasingly strict control of sulfur and nitrogen compounds in all fuels, particularly those that are carcinogenic. Attention will also be given to the hydrogen content of fuels because of its

PROJECTION OF THE PETROLEUM SUPPLY

The annual world production of petroleum is expected to continue to outrun discovery rate during the 1980s and beyond (Figure 1). Taking into account the discovery rate of new reserves and the rate at which available reserves are used, the production rate will begin to limit consumption increasingly severely between 1980 and 2000, with the severity depending on OPEC pricing and production policies (Figure 2).

With the supply of petroleum becoming limited and its price increasing, we should soon begin to see the replacement of liquid fuels with other forms of energy where practical. In stationary equipment, we can expect a switch to solid and gaseous fuels, electricity, and solar energy. In the transportation sector, however, the reliance on liquid fuels is likely to continue for at least 25-50 years with some use of electricity in public transport and automotive systems (General Motors, 1974; Sheridan et al., 1976; National Research Council, 1979).

A wide variety of predictions of future petroleum use is available (Dupree and Corsentino, 1975; U.S. Department of Commerce, 1977; National Research Council, 1980). The values used here presume a reasonably orderly world economic system and a drive for conservation tempered by economic considerations and a general reluctance to drastically change present lifestyles. The values imply, for example, a slow phase-out of oil use in power generation, allowing the normal retirement of oil-burning power plants; they also assume a less drastic reduction of fuel use in automobiles than is found in the more extreme forecasts.

An examination of recent U.S. trends in the use of petroleum fuels should help provide an insight into whether other energy forms can be substituted for liquid fuels and, if not, the kinds of non-petroleum fuels that may be required. This is done in Chapter 3.

As the current surplus refining capacity for petroleum-derived fuels becomes supply-limited, the price of petroleum should increase relative to those of other commodities; liquid fuels from shale and coal might then then become an efficient and economical supplement.

MAXIMIZING EFFICIENCIES

With petroleum fuels, the emphasis in efficiency improvement has been placed on the end user because of the relatively low expenditure of

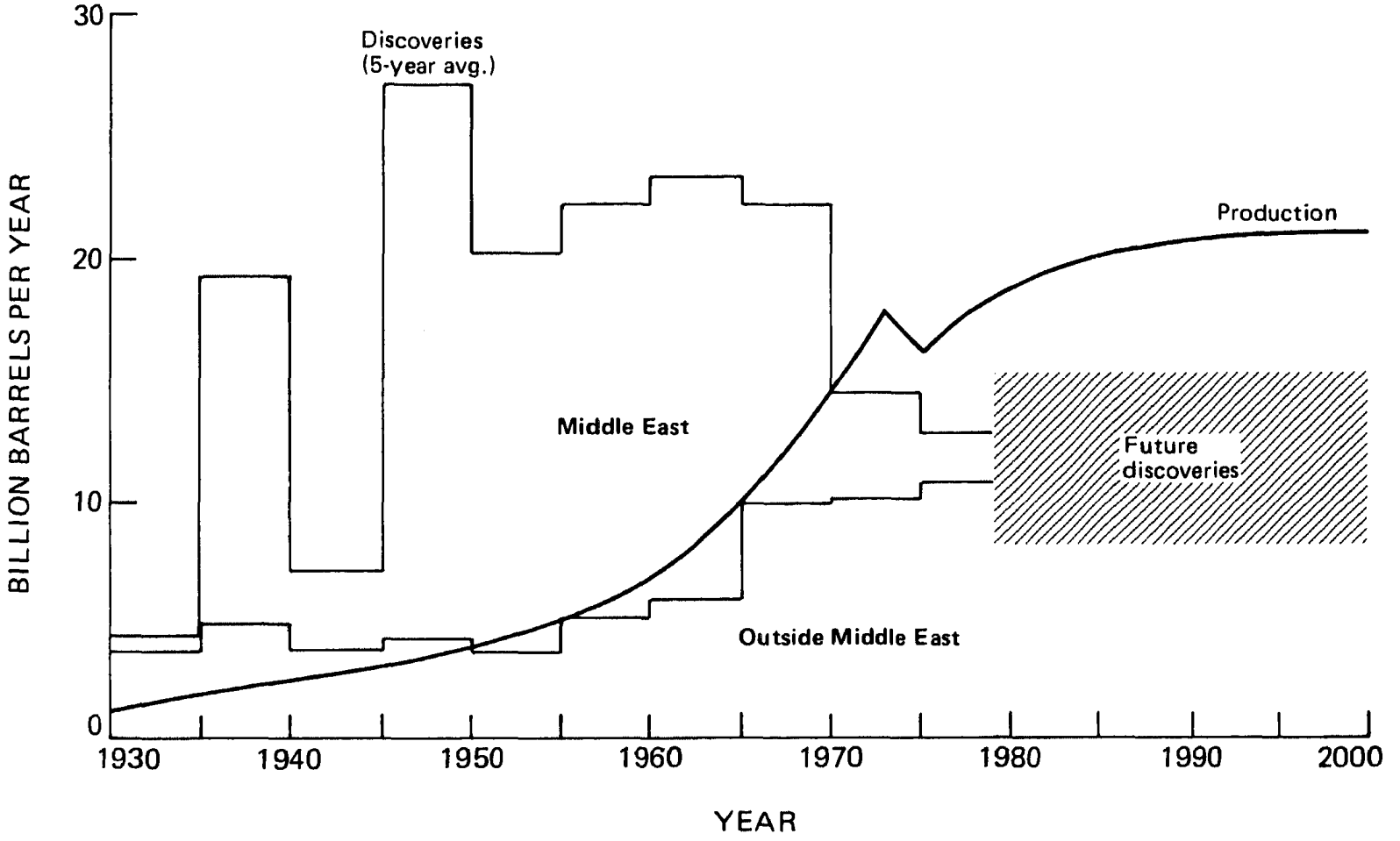


Figure 1 World oil discovery and production rates from 1930 to 2000, excluding the People's Republic of China, the Soviet Union, and Eastern Europe (Exxon, 1980)

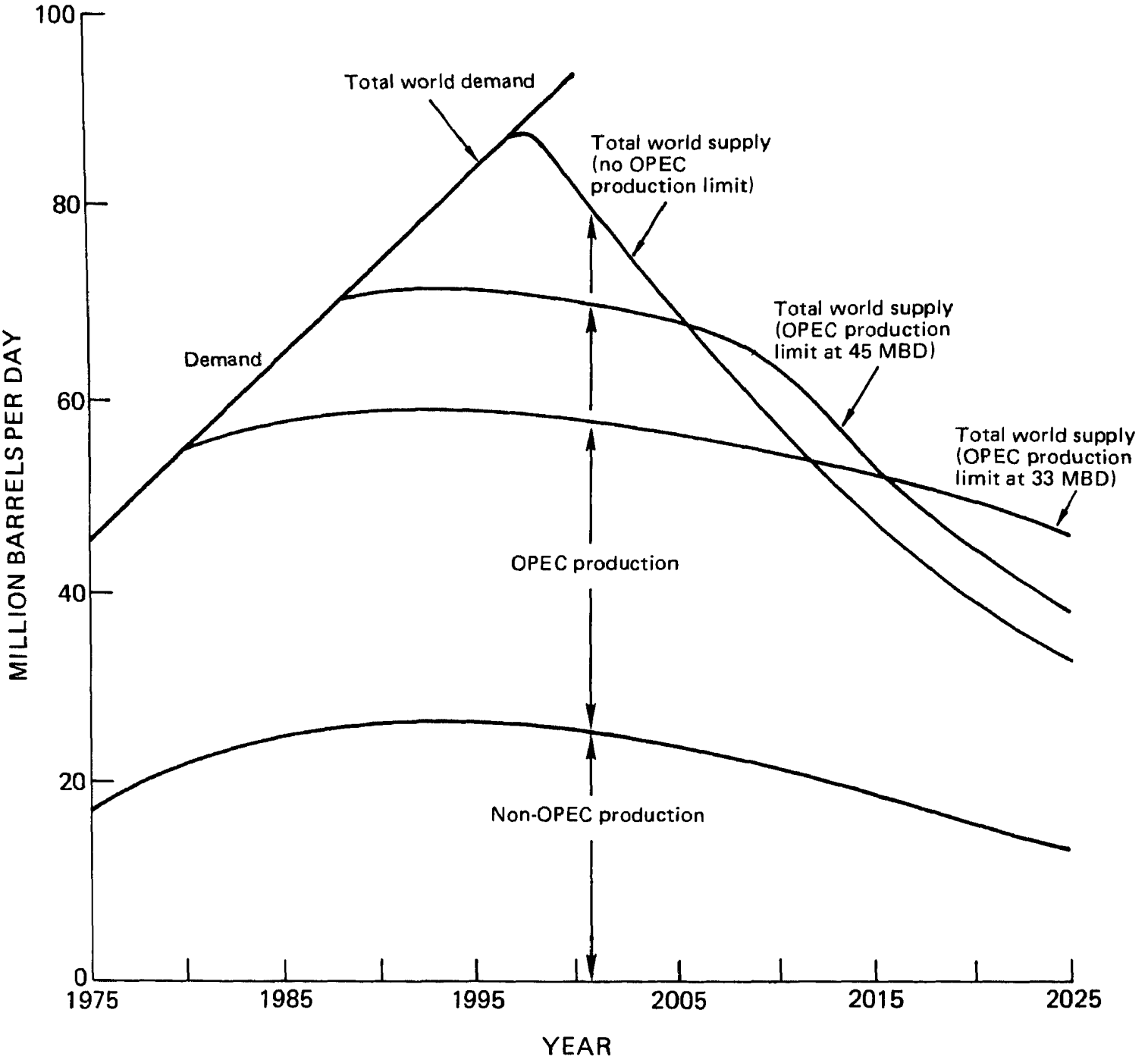


Figure 2 Projections of world petroleum demand to 1999 and supply to 2025 (Workshop on Alternative Energy Strategies, 1977)

energy involved in removing crude oil from the ground, delivering it to the refinery, refining it, and distributing the products to users. The emphasis will change dramatically as we shift from petroleum to oil shale and coal as sources of liquid fuels for transportation. The estimated conversion efficiencies (the percentage of the Btu's in the original feeds that remains in the products) for producing liquid fuels from oil shale and coal are substantially lower than those involved in using petroleum as a source (Figure 3). The energy expended for a given output can vary greatly, depending on the sulfur, nitrogen, aromatic, and ash contents of the coal and shale liquids, as well as their distillation properties and the degree to which these liquids are refined. This also raises the possibility of increasing the overall energy efficiency by modifying or developing engines and stationary combustion systems for the use of shale and coal liquids in the "least

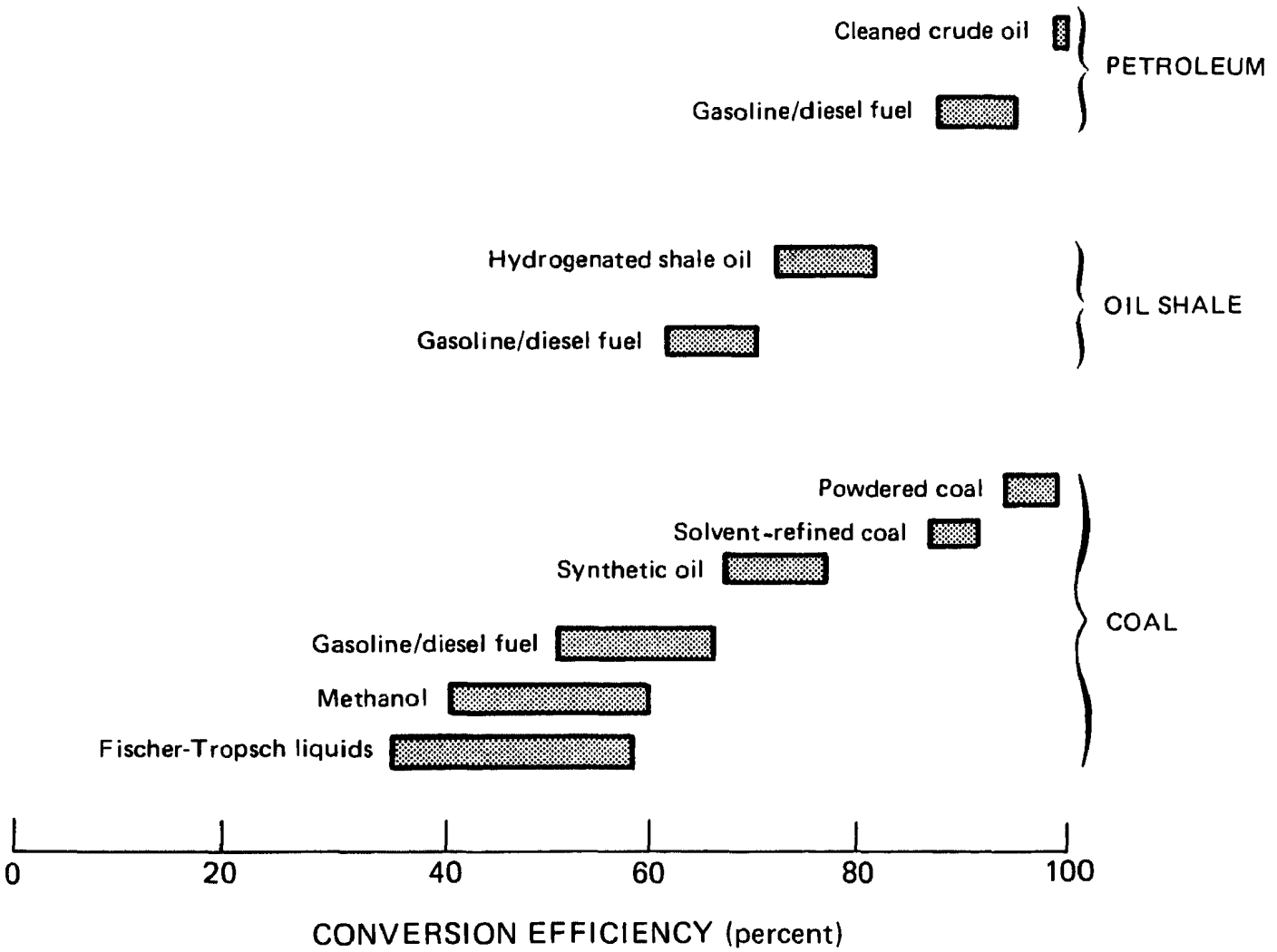


Figure 3 Estimated conversion efficiencies in producing liquid fuels

of complying with existing federal and state regulations, especially those relating to emissions.

LIQUID FUELS FROM OIL SHALE AND COAL

Pioneer production of coal and shale liquids is expected to begin in the mid-1980s, with substantial production by the end of the century. By the year 2025, there is the possibility that half of the U.S. liquid fuel production will come from these sources. While such predictions cannot be made with any precision, it is nevertheless clear that it will be some time before important quantities of liquid fuel are derived from coal and shale.

There are major differences among the various crude liquids obtained from coal and shale. One is hydrogen content. The atomic hydrogen/carbon (H/C) ratios for coal liquids vary between 1.0 and 1.2, and the atomic H/C ratios for shale oil and petroleum crudes vary between 1.6 and 1.8. Typical liquid fuels in use today fall in the 1.7-1.9 range. While the relatively low hydrogen contents of aromatic fuels may be advantageous for use in engines that require higher octane gasolines, diesel engines and home heating furnaces have difficulty burning fuels in which the H/C ratio is low. Hydrogen can be added to coal liquids to increase the H/C ratios, but this is expensive and wasteful of energy. The thrust of future technology will be toward a more efficient use of hydrogen to achieve a given product composition.

As coal and shale liquids come into use, they will replace petroleum in different applications with varying degrees of suitability, as indicated in Table 1. Petroleum will, of course, be best suited for all its present uses, since these were developed around petroleum, but petroleum components now used for heavy fuel oil will be converted to more highly refined products (e.g., aliphatic petrochemicals and olefins for plastics); these can be produced more economically from the heavier petroleum components than from shale and coal liquids. Coal liquids, because of their high aromatic contents, will be excellent sources of gasoline and could be preferentially used for this purpose; their low hydrogen contents will also make them useful for the production of heavy fuel oil. Shale liquids will generally fit the same use patterns as petroleum and should be useful for the production of jet and diesel fuels.

Coal or coal char can also be converted to a CO/H_2 mixture which can, by catalytic conversion, be made to yield a variety of hydrocarbons, alcohols, and chemicals. If fuels high in hydrogen are required from coal, this "indirect" liquefaction might provide the most appropriate route. Aromatic gasoline components can also be produced by

	Gasoline	Jet and diesel fuels	Other distillate fuels	Heavy fuel oils	Aliphatic petro-chemicals
Petroleum	X	XX	X	X	XX
Shale oil	X	XX	X	X	X
Coal liquids	XX	O	O	XX	O
CO/H_2-based liquids	XX	XX	X	O	X

[a]XX: very well suited; X: well suited; O: poorly suited.

The total refining capacity in the United States is not considered likely to increase appreciably for a number of years. There will be little incentive to build expensive new refineries since it should be possible to convert a refinery from petroleum to coal and shale liquids with the addition of hydroprocessing and other facilities. After appropriate feed hydrotreating, existing petroleum conversion and separation processes can also be used for coal and shale liquids.

BIBLIOGRAPHY

Dupree, W. G., and J. S. Corsentino. 1975. United States Energy Through the Year 2000. Revised. Bureau of Mines. Washington, D.C.: U.S. Department of the Interior.

Exxon Corporation. 1980. World Energy Outlook. Exxon Background Series (December 1979). New York: Exxon Corporation.

General Motors Corporation. 1974. Energy Utilization Comparison of Gasoline and Battery-Electric Powered Urban Vehicles. Detroit: General Motors (Research Publication GMR-1978).

Kant, F. H., R. P. Cahn, A. R. Cunningham, M. H. Farmer, and W. Herbst.

and Alternative Energy Systems. Washington, D.C.: National Academy of Sciences.

National Research Council. 1980. Energy in Transition, 1985-2010. Committee on Nuclear and Alternative Energy Systems, National Research Council. San Francisco: W. H. Freeman and Co.

Pangborn, J., and J. Gillis. 1974. Alternative Fuels for Automotive Transportation--A Feasibility Study. Vols. 1-3. Institute of Gas Technology. Washington, D.C.: U.S. Environmental Protection Agency (EPA-460/3-74-012-2-b,c).

Sheridan, D. C., J. J. Bush, and W. R. Kuziak, Jr. 1976. A Study of the Energy Utilization of Gasoline and Battery-Electric Powered Special Purpose Vehicles. Warrendale, Pa.: Society of Automotive Engineers (SAE Paper 760119).

Stebar, R. F., W. A. Daniel, A. R. Sapre, and B. D. Peters. 1977. Matching Future Automotive Fuels and Engines for Maximum Energy Efficiency. In Future Automotive Fuels, ed. J. M. Colucci and N. E. Gallopoulos, pp. 96-120. New York: Plenum Press.

U.S. Department of Commerce. 1977. Forecast of Likely U.S. Energy Supply/Demand Balances for 1985 and 2000 and Implications for U.S. Energy Policy. Domestic and International Business Administration. Springfield, Va.: National Technical Information Service (PB-266240).

Workshop on Alternative Energy Strategies. 1977. Energy: Global Prospects 1985-2000. New York: McGraw-Hill.

3 FUTURE PRODUCT REQUIREMENTS

onpetroleum fuels have been considered for transportation many times in he past. Germany produced liquid fuels from coal during World War II nd South Africa is doing so today. Oil has been produced from shale n the Soviet Union, Scotland, Brazil, and elsewhere. It is now quite lear that a major effort must be mounted to prepare the United States or the production and use of these fuels during the rest of this century.

In evaluating what must be done to adapt the transportation system n the United States to the use of liquids from coal and/or oil shale, a umber of questions must be answered.

- What kinds of liquid fuels will be required during the years ahead? This question can be answered by examining the types of engines and vehicles that will use these fuels. Most of the engines now in use are spark-ignition and compression-ignition (diesel) engines. The conventional fuels used by these engines are gasoline and diesel fuels, both produced from petroleum. New fuels that can be produced from petroleum, coal, and oil shale will be suitable for today's engines only if they closely resemble the gasoline and diesel fuel currently in use. If they differ, however, they may still be usable in modified versions of current engines as well as in unconventional engines such as gas turbines, Stirling engines, and some stratified-charge engines.

- How will the new fuels be introduced? Will the liquid fuels produced from coal and shale be intended for use with conventional as well as new engines, or will they be intended only for use in new engines? If the former is the case, it may preclude radical changes in fuel quality or composition that might allow the overall optimization of costs and energy use. If the latter is the case, it would require the development of new engines and vehicle systems, limiting the rate at which the new fuels could be put to use.

- To what extent can liquid fuels derived from coal and oil shale be substituted for petroleum fuels now used for residential and industrial purposes and for electricity generation by utilities?

Electric Power Generation

Liquid fuels now used for electric power generation consist mainly of high-boiling-point (No. 6) fuel oil. While this petroleum fraction contains none of the lower boiling fractions used in the major transpo tation systems, modern refining technology can convert the high-boilin fraction to clean lower boiling fractions more efficiently than it can refine coal and shale liquids. As the liquid fuel demands of transpor tion increase over the years ahead, we will very likely see a shift of petroleum use from the utilities to transportation, with oil shale and coal providing the fuel for electric power generation. Coal, of cours can be used directly as a utility fuel, but converting existing plants from liquid and gaseous fuels to coal is difficult and expensive. Ele tric power plants now in operation may be able to switch to relatively unrefined coal liquids and shale liquids more easily than they can switch to coal. The use of liquid fuels makes it easier to meet emiss standards.

With new power plants the situation is different. In a new plant coal and nuclear energy offer the advantage of being more economical than liquid fuels.

The Industrial Sector

The oil now used for industrial purposes is, like utility fuel, compos largely of the higher boiling fractions. The trend in the energy cons ing industries will be much like that in the utilities. The use of oil will peak over the near term as it replaces gas and then decline as it, in turn, is replaced by coal.

The Buildings Sector

In commercial and residential buildings, the replacement of gaseous an liquid fuels with coal is not generally practical; the trend toward electric heating will result in the greater use of coal and nuclear power, however. The use of liquid fuels in buildings will therefore level off or slowly decline over the next two decades.

Nonenergy Uses

In contrast to fuel use, the nonenergy use of petroleum and other liqu hydrocarbons (as petrochemical feedstocks, asphalt, etc.) is expected to grow rapidly. For example, the use of plastics to reduce the weigh of automobiles should increase, resulting in a lower use of petroleum

Because of its composition, shale oil is a possible substitute for petroleum in the production of olefins for plastics. Coal would have to be put through drastic conversion processes to produce the monomers needed for plastics (e.g., gasification followed by Fischer-Tropsch synthesis).

The Transportation Sector

The quantity of liquid fuel used in the transportation sector is a major percentage of the total quantity produced. While this percentage will decline over the near term, it may increase slowly after 1990 as the increasing use of liquid fuels by trucks and airlines more than makes up for the decline in fuel use by passenger cars.

The future use of fuels by automotive vehicles will depend on the following variables:

- Fuel economy standards for passenger cars, light-duty trucks, and heavy-duty trucks[a]
- The mix of fuels (gasoline or diesel oil) used by each class of vehicles
- The number of miles traveled per year by each vehicle
- The number of vehicles in use
- Vehicle sales and scrappage rates.

Recent forecasts of gasoline demand are shown in Figure 4. There appears to be a general consensus that gasoline consumption will decline during the 1980s as a result of the mandated fuel economy standards. Forecasts have not been made beyond 1990 because of the uncertain nature of the standards that might be mandated beyond 1985.

Two important points should be made about the gasoline demand projections in Figure 4:

- These projections indicate trends; they should not be considered immutable.

---

[a]Federal standards for the fuel economies of passenger cars have been established through 1985. Standards for the fuel economies of light-duty

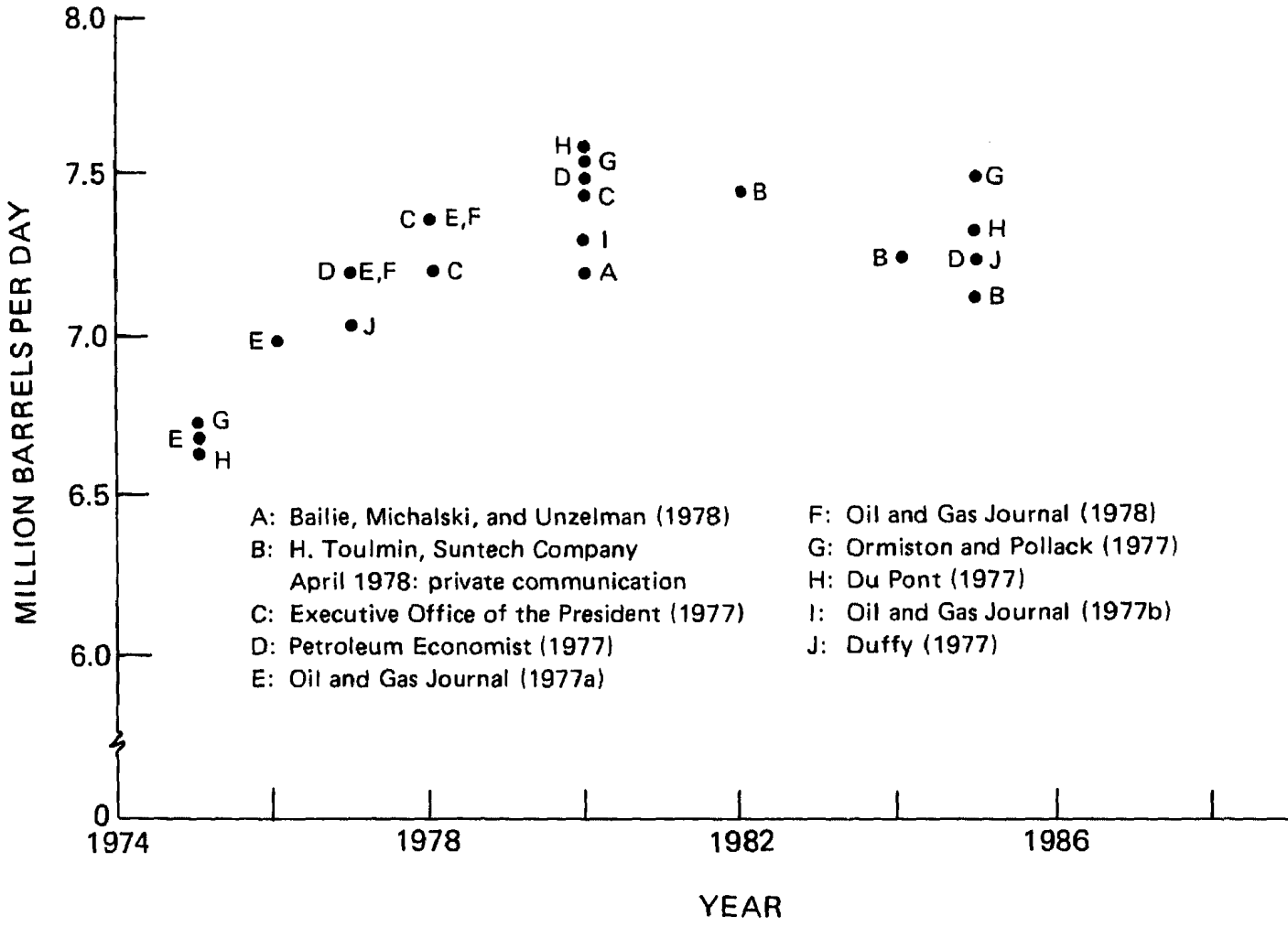


Figure 4 Selected forecasts of U.S. gasoline demand to 1990, in
lions of barrels per day

will be needed to meet federal emission standards. Gasoline used by heavy-duty trucks will probably be leaded as long as emission standards do not preclude its use, but most heavy-duty trucks will probably continue to be built with diesel engines.

The increasing use of diesel engines in heavy-duty trucks, the trend toward diesel-powered passenger cars and light-duty trucks, and the continued use of distillate fuels in trains and aircraft will result in a greater demand for distillate fuels in the future, affecting the gasoline/mid-distillate fuel ratios required from petroleum and nonpetroleum resources.

Projections of fuel use by aircraft vary widely, but it is generally agreed that fuel use in this mode will grow more rapidly than in the other transportation modes.

TYPES OF LIQUID FUELS REQUIRED

The discussion of fuel types can be simplified by dividing them into three major categories, according to their boiling points (Table 2).

Heavy Fuel Oils

The heavy fuel oils are the least refined of liquid fuels. Shale and coal liquids may require the removal of organic nitrogen. The higher boiling fractions must be used in installations where human contact can be carefully controlled, because of their substantially higher carcinogenicity (particularly in the coal-based liquids and the intensely pyrolyzed petroleum-based fractions). The use of heavy fuel oil is now rising rapidly but is expected to fall considerably in the future as it

Table 2 Boiling ranges of fuel types

Fuel types	Boiling range (^{o}F)
Heavy fuel oils	700+
Mid-distillates	350-700
Gasoline	80-440

and gasoline. (The allow
No. 6 fuel oil from petroleum are outlined in Table 3.)

Mid-Distillates

This category consists primarily of kerosene, jet fuel, diesel f
and No. 2 (domestic) heating oil. The initial boiling point is
safety considerations and is defined by a "flash point" specifi
that ranges between 100°F and 140°F, depending on the applicati
The final boiling point has historically been determined by free
point or viscosity considerations, since these fuels are used du
the winter and are stored outside.

Kerosene and jet fuel must, at present, have high hydrogen
to reduce soot formation, in current combustion equipment. This
ment results in an aromatic content specification under 25 perce
The hydrogen content of diesel fuel need not be so high, but it
high enough for easy ignition in passenger car and truck engines
limits the aromatic content to around 35 percent. Home heating
(No. 2) requires still less hydrogen, but in current practice is
duced with an aromatic content only slightly (5-10 percent) high
that of diesel fuels to avoid problems with soot and smoke forma

In all cases, the nitrogen content must be kept low to avoi
and deposits during storage and use. The sulfur content must be
below 0.5 percent to meet current SO_x emission standards.

Gasoline

Although there is some overlap in the boiling ranges of gasolin
mid-distillates, gasoline is basically a volatile fuel that perm
cold starting and reasonably complete evaporation before ignitio
a result of the high vapor pressure of its lower molecular-weigh
ponents. Unlike mid-distillate performance, gasoline performanc
improved by the inclusion of aromatics; consequently, much of mo
gasoline refining technology centers on the conversion of paraf
naphthene into high-octane aromatics.

The conversion requirements of a refinery are determined by
line/mid-distillate ratio. In the past, the large demand for ga
the United States has dominated production, the demand for mid-d
being relatively easy to meet from naturally occurring petroleum
tions and products incidentally produced during gasoline product

This balance is expected to change drastically in the futu
the end of the century approaches and the rising demand for mid-

Combustion Properties

- Coal liquids produce fewer large particulates because fuel can vaporize during combustion.
- Coal liquids have a greater tendency to form soot because of their lower hydrogen contents.
- Coal liquids produce a more luminous flame due to their lower hydrogen to carbon ratio; this produces a different heat transfer balance.

Emissions

- Coal liquids contain less sulfur than most unprocessed petroleum fuel oils.
- Coal liquids produce more NO_x because of their higher organic nitrogen content (0.5-1.5 percent compared to 0.1-0.5 percent for petroleum-derived fuel oil).
- Conventional oil-burning equipment will generally exceed NO_x and particulate emission standards when using coal liquids, but control technology is being developed.

Toxicity

- Coal-based fuel oils contain higher concentrations of skin carcinogens than virgin petroleum and will probably require special handling.

Stability

- Coal liquids tend to polymerize and increase in viscosity during storage.
- Deposits in atomizing nozzles are a greater problem with coal liquids.

Compatibility

- Since mixtures of petroleum-based and coal-based fuel oils form precipitates, separate storage and handling facilities will be required.

Table 4 gives a projection of changes in the gasoline/mid-distillate fuel ratio, assuming moderate use of diesel engines in passenger cars. Major substitution of diesel engines for gasoline engines could bring a gasoline/mid-distillate ratio as low as 0.6 by the year 2000.

The large shift in this ratio over the years ahead should make it basically easier to meet the demand for high-aromatic, high-octane gasoline (assuming paraffinic naphthas can be used as petrochemical feedstocks). Meeting the demand for high quality mid-distillates, on the other hand, will become increasingly difficult and expensive because hydrogen-consuming processes (e.g., hydrocracking and hydrogenation) will be required. The future would be difficult even if sufficient quantities of petroleum were available as the major refinery feed; the switch to low-hydrogen coal and shale liquids will make the production of conventional mid-distillates even more difficult.

The higher cost of tailoring coal-derived and shale-derived fuels to end-use equipment designed for petroleum products will provide a major incentive to the development of end-use equipment capable of burning low-hydrogen mid-distillates cleanly. Along with this will come the need for refining technology optimized for producing these fuels.

Table 4 Projection of future gasoline/mid-distillate ratios

Year	Gasoline/mid-distillate ratio
1975	1.7
1980	1.5
1990	1.2
2000	1.0
2000+	0.5-1.0

Source: Shearer and Wagner (1977).

ethanol will offer additional options for adjusting the match be-
n fuel production and consumption.

FUTURE TRANSPORTATION FUELS

problems likely to be met in developing nonpetroleum fuels for
in transportation during the years ahead are discussed under the
owing headings.

Gasoline

line and the spark-ignition (Otto cycle) engine have evolved to
r current forms over a period of time. The process has been one of
al adaptation as gains were made with one or the other, or as re-
ements changed (e.g., the need for unleaded gasoline when emission
dards necessitated the use of catalytic converters). The mutual
tation between engines and fuels will very likely continue as non-
oleum fuels come into use.

The standards currently specified by the American Society for Test-
and Materials for automotive gasoline, given in ASTM D 439-79, do
completely define gasoline but, rather, describe various characteris-
of gasolines for use in cars, trucks, and buses over a wide geo-
nical range.

The key properties described in ASTM D 439-79 for gasoline are the
owing:

- Octane quality (including the concentration of antiknock additives)
- Vapor pressure
- Vapor-liquid ratio
- Distillation characteristics
- Oxidation stability
- Corrosion characteristics
- Existent gum
- Sulfur content.

mers and may be precursors in the generation of polynuclear aromatic hydrocarbons during combustion (although this may not be a problem for engines equipped with catalytic converters).

Diesel Fuel

Diesel engines, now used primarily in trucks, buses, trains, tractors, and stationary engines, may begin to find increasing use in passenger cars as the automotive industry attempts to comply with federally mandated fuel economy and emission standards. Like gasoline, diesel fuels have evolved through the mutual adaptation of fuels and engines over a long period of time, and this interaction will undoubtedly continue when nonpetroleum fuels are introduced.

The standards currently specified for diesel fuel in ASTM D 925-77 are not a complete definition but, like the ASTM standards for gasoline, describe the characteristics required for the use of this fuel under a wide range of conditions. The key diesel fuel properties described in ASTM D 925-77 are as follows:

- Cetane quality
- Distillation characteristics
- Viscosity
- Carbon residue
- Sulfur content
- Flash point
- Cloud point
- Ash content
- Copper strip corrosion.

Nitrogen content will become an important property when diesel fuels are produced from oil shale and coal, since there are indications that high nitrogen contents degrade the stability of diesel fuels and raise the tendency to form acids.

Aviation Fuel

lower freezing point (-54°F, as against -40°F). The lower freezing point makes the new fuel more difficult to produce.

The amount of jet fuel needed at present can be supplied without difficulty, generally, but the demand is approaching the point at which it could interfere with the production of other mid-distillate products. An increase in jet fuel demand together with an increase in diesel fuel demand will tend to force the use of cracked stocks with higher aromatic contents. The cost and complexity of producing jet fuel over the years ahead could be eased considerably by raising the freezing point (allowing the inclusion of components with higher boiling points) and decreasing the hydrogen content requirement. The latter would be helpful when coal and shale liquids need to be used.

With air transportation particularly vulnerable to the cost and supply of fuel, there is much to be gained from examining the trade-offs involved in the development of aircraft that can use fuels with less stringent specifications. To allow laboratories and contractors to focus on the research, development, and design problems involved in optimizing fuel/aircraft combinations for the future, NASA held a workshop in June 1977 (National Aeronautics and Space Administration, 1977) at which specifications for a new jet fuel for research purposes were agreed upon by representatives of the airlines, the airframe and engine industries, the fuel producers, and various government agencies. The characteristics of this fuel, designated as Experimental Referee Board-Specification (ERBS) jet fuel, are listed in Table 5.

One of the most important changes made was a reduction of the hydrogen content to 12.8 percent; the aromatic content of 35 percent is substantially different from the specified 20-25 percent for Jet A. This change will allow the use of cracked petroleum stocks and materials manufactured from coal and shale, greatly improving the flexibility of jet fuel manufacture.

The second most important change was the raising of the freezing point from -40°F to -20°F, allowing the use of higher boiling point components than those used to produce Jet A and further increasing the flexibility of manufacture.

The characteristics of ERBS jet fuel approach those of a high-quality diesel fuel, but the severe thermal stability requirements will necessitate hydrotreating and the almost complete removal of organic nitrogen. The hydrotreating processes now available will be adequate when petroleum is used as a base, but more efficient processing will be desirable when coal and shale liquids are used to produce this fuel.

The introduction of a low-hydrogen fuel like ERBS jet fuel will

comparison

Specifications	ASTM Jet A	ERBS Jet Fuel	Prop test
Composition			
Hydrogen, wt %	--	12.8±0.2	NM
Aromatic carbon, vol %	25 max	Report (35 typical)	ASTM
Sulfur, wt %			
Mercaptan	0.003 max	0.003 max	ASTM
Total	0.31 max	0.3 max	ASTM
Nitrogen, wt %	--	Report	Kjel
Naphthalenes, vol %	--	Report	ASTM
Hydrocarbon compositional analysis	--	Report	G.C.
Volatility			
Distillation temperatures, °F			
Initial boiling point	--	Report	ASTM
10%	400 max	400 max	
50%	450 max	Report	
90%	--	500 min	
End point	550 max	Report	
Residue, percent	1.5 max	Report	
Loss, percent	1.5 max	Report	
Flashpoint, °F	105-150	110±10	ASTM
Gravity, °API at 60°F	39-150	Report	ASTM
Gravity, specific (60/60°F)	--	Report	ASTM
Fluidity			
Freezing point, °F	-40	-20 max	ASTM
Viscosity, cSt[a] at -10°F	--	12 max	ASTM
Net heat of combustion, Btu per pound	18,400 min	Report	ASTM
Thermal stability[b]			
Breakpoint temperature, °F	--	460 min	ASTM

[a]Centistokes.

ERBS-type jet fuel will very likely preclude its use in the present fleet. The new fuel must be considered for use over the long term as the next generation of aircraft comes into use. If it is decided not to proceed with the new fuel, the production of the present type of jet fuel from oil shale and coal will require the introduction of hydrogen-intensive processing or, in the long run, the synthesis of paraffinic Fischer-Tropsch liquids from coal.

FUTURE AUTOMOTIVE ENGINES AND THEIR FUEL NEEDS

Table 6 lists a variety of future engine possibilities and their potentials for use in passenger cars, trucks, and farm machinery. Table 7 indicates the relaxation in fuel properties that may be possible with these engines.

A brief discussion of the fuel requirements for each of the engines follows.

Homogeneous-Charge Spark-Ignition Engine (Carbureted)

Since a decrease in the volatility of gasoline impairs vehicle performance, no significant reduction in volatility can be permitted in substitute fuels for carbureted spark-ignition (SI) engines. If a separate fuel and fuel system were used for cold starting, front-end volatility requirements for the main fuel might be relaxed somewhat, but mid-range and back-end volatility similar to that for present-day gasoline would still be required. Dual-fuel systems have never proven practical, however.

The need to maintain fuel octane quality at or near the present level will place an additional strain on the fuel industry over the near term. As it is now, the unleaded octane pool needs to be increased to at least a 91 research octane level from its current level of 88-89 because new cars and light-duty trucks are being designed to use 91 octane fuel.

If spark-ignition engines continue to be designed for this type of fuel, gasoline feedstocks derived from coal and shale liquids will have to be capable of providing the required octane quality. The high aromaticity of coal-derived materials is expected to make it possible to use them for the production of high-octane gasoline if the systems exposed to the fuel are designed with elastomers and other materials that are impervious to aromatics. The high aromaticity of gasoline from coal may make it possible to design more efficient engines with higher octane requirements than those of today (Longwell, 1978).

Engine	Small passenger cars	Large passenger cars and small trucks	Heavy trucks and large farm machinery
Homogeneous-charge spark-ignition	XXX	XX	0
Diesel	XX	XXX	XXX
Direct injection stratified-charge	XX	X	X
Gas turbine	0	X	XX
Stirling	X	XX	X

[a]XXX: significant number; XX: moderate number; X: low number; 0: none. Underscore indicates engine currently used in this application.

The need to maintain high octane quality and volatility may preclude major changes in other properties of synthetic fuels, however. Octane and/or volatility requirements may, for example, limit the extent to which the viscosity might be increased. This difficulty could be dealt with by redesigning carburetors, provided the variations between batches of fuel are not excessive. New fuel metering systems, such as the computer-controlled, low-pressure throttle-body injection systems introduced in 1980 and 1981 model cars, may further increase the spark-ignition engine's flexibility in handling fuels of varying viscosity and volatility.

A somewhat higher nitrogen content in a synthetic fuel could probably be handled within the constraints of present emission standards and engine durability requirements, but very high nitrogen and sulfur concentrations in coal and shale liquids may introduce difficulties in the refining processes, just as in the refining of petroleum.

Homogeneous-Charge Spark-Ignition Engine (Timed Fuel Injection)

Fuel volatility requirements may be reduced in timed-fuel-injection engines. In a carbureted engine, the fuel must be volatile enough to

proper distribution of fuel to each of the cylinders. The timed high pressure injection of fuel into each inlet port or cylinder in a fuel-injection engine reduces the distribution problem but a certain degree of front end volatility is still necessary for starting a cold engine. A separate starting fuel of high volatility would allow the volatility specification of the main fuel to be greatly relaxed, but dual-fuel systems have not proven practical to date.

The viscosity of a fuel could be greater and more variable for a fuel-injection engine than for a carbureted engine, but the fuel octane quality would need to be maintained. This could effectively limit an increase in viscosity and decrease in volatility for synthetic fuels, as it does in most cases for petroleum-derived fuels.

This engine's ability to tolerate the higher concentrations of nitrogen, sulfur, ash, and aromatics in synthetic fuels will be the same as that of the carbureted spark-ignition engine, and the same potential interactions of these properties with octane quality would apply.

Compression-Ignition (Diesel) Engine

Diesel engines can use fuels with a wider range of properties than spark ignition engines. Although there is evidence that smoke, particulates, odor, and hydrocarbons increase with lower fuel volatility, the engine could probably tolerate less volatile fuels. The sulfur content of diesel fuels approaches the one percent level in some foreign countries and has been associated with accelerated engine corrosion and wear. As indicated earlier, high nitrogen levels can cause problems.

A high ash content in synthetic diesel fuels would be undesirable, because it could not only increase combustion chamber deposits and contribute to particulate emissions but also clog fuel injectors.

The ignition quality (cetane index) of future diesel fuels should remain at or near current levels, particularly for fuels used in the high-speed diesels produced for passenger cars and light-duty trucks. High aromatic levels can be tolerated in diesel fuels, but they generally decrease ignition quality and increase exhaust smoke.

An increase in viscosity may degrade fuel atomization in the combustion chamber, but higher injection pressures likely in future engines, particularly in open-chamber designs, should counteract the effects of higher viscosity in fuels derived from coal and shale. The lubricity of diesel fuels should remain high to protect fuel-injection system components.

Conventional Engines			
Homogeneous-charge SI engine (carbureted)	Current gasoline	No change	Higher
Homogeneous-charge SI engine (fuel-injected)	Current gasoline	Lower	Higher
Compression-ignition engine (diesel)	Current diesel fuel #1 or #2	Lower	Higher
Unconventional Engines			
DISC (PROCO) engine (stratified-charge)	Current gasoline	Lower	Higher
DISC (Texaco) engine (stratified-charge)	Distillate, current gasoline[d]	Lower	Higher
Gas turbine	Distillate, current gasoline[d]	Much lower	Much higher
Stirling engine	Distillate, current gasoline[d]	Much lower	Much higher

[a]Assuming "tolerable" relaxations in the properties of future fuels relative to the properties of "desirable fuels." There are reasons to believe that changing fuel properties in the directions indicated may result in an increase in overall energy efficiency; no energy savings would be anticipated for property changes in the opposite direction, and energy losses would probably result.

[b]Cetane rating.

[c]Higher sulfur content could adversely affect performance of catalytic emission control systems, especially the new three-way catalyst systems.

[d]Broad-cut distillate, diesel fuel, kerosene, or jet fuel.

Fuel characteristics					
Aromatic content	Impurity Content			Octane rating	Ignition quality[b]
	Sulfur	Nitrogen	Ash		
Higher	Higher[c]	Higher	No change	No change	--
Higher	Higher[c]	Higher	No change	No change	--
Higher	Higher	Higher	No change	--	No change
Higher	Higher	Higher	No change	Lower	--
Higher	Higher	Higher	No change	None required	None required
Higher	Much higher	Much higher	Higher (not heavy metals)	None required	None required
Higher	Much higher	Much higher	Higher	None required	None required

used to achieve stratification of the fuel-air mixture. Although diesel engines incorporate charge stratification, this discussion is limited to spark-ignition engines.

The stratified-charge spark-ignition engines on the road today use a prechamber to separate the rich mixture (where combustion is initiated) from the remaining lean mixture. The fuel requirements of these engines are not significantly different from those of the spark-ignition engines already discussed.

Stratified-charge engines in which fuel is injected into an undivided combustion chamber have the potential for tolerating a wider range of fuel properties than other spark-ignition engines, however. There are two distinct types of engines in this direct-injection category, described next. Neither is available to the public in production automobiles.

Direct-Injection Stratified-Charge (DISC) Engine (PROCO)

In the PROCO ("programed combustion") engine undergoing development by the Ford Motor Company, the fuel is injected halfway through the compression stroke into a high-intensity swirl set up during the air-intake stroke, and the fuel-air mixture ends up (toward the end of the compression stroke) in a cup in the piston where it is ignited. With the relatively high turbulence in the fuel-air mixture, it burns rather quickly and, as a result, detonation (knocking) does not occur at the compression ratios at which it begins to be a problem in conventional spark-ignition engines. Instead of using this feature to lower the octane requirement of the engine, the PROCO engine takes advantage of it by raising the compression ratio to about 11:1, thereby increasing the power output for a given engine displacement and increasing the efficiency of energy use.

The other fuel property requirements for this engine are about the same as for other direct-injection spark-ignition engines.

Direct-Injection Stratified-Charge (DISC) Engine (Texaco)

This engine has been undergoing development by Texaco (and others) for more than 30 years. A high-velocity air swirl set up in the cylinder during induction persists through the compression stroke and, as the piston nears top center, is compressed into a cup in the piston. When fuel is injected into the air (in the same direction as the swirl), a combustible mixture forms almost immediately at the edges of the spray where ignition is initiated (by a spark gap located just downstream of

The problem of unreliable spark ignition that has sometimes been observed with this type of engine cannot be attributed entirely to the properties of the fuel. The degradation in performance of the fuel-injection and spark-ignition systems and the difficulties encountered in operating over wide ranges of engine speed and load are more likely causes. Since all portions of the fuel-air mixture are burned essentially as soon as they are formed, no end gas region exists and the engine has no octane requirement. Since a high-energy spark minimizes ignition delay, the engine has no cetane requirement. Other fuel property requirements are about the same as for the diesel engine.

Open-Cycle Gas Turbine

The open-cycle gas turbine has no octane or cetane requirements. It can use a wide range of fuels; the only essential requirement is that the fuel flow adequately at the lowest temperature encountered in service. Since a relatively long time is available for ignition at start-up (far more than that available during each cycle of a diesel or spark-ignition engine), fuel volatility is relatively unimportant.

The gas turbine can also tolerate significantly higher quantities of impurities (e.g., nitrogen, sulfur, and ash) than those in current automotive fuels and still operate within the constraints of exhaust emission standards, although higher contents of heavy metals could increase corrosion.

Fuels with a high aromatic content would cause higher combustor skin temperatures (because of the increased radiation from the flame) as well as increased soot and smoke formation, but these problems can be solved by redesigning the combustor.

External Combustion Engines: Stirling, Rankine, and Closed-Cycle Gas Turbine Engines

These continuous-combustion engines should be able to burn any liquid hydrocarbon fuel that can flow adequately at the lowest temperature encountered in service.

SURVEY ON COMPATIBILITY OF FUTURE AUTOMOTIVE FUELS AND ENGINES

To obtain some insight into the problem of matching fuels to engines, letters were sent to a representative group of experts in automotive and

Summary of the comments received.

There was no unanimity on whether "less refined" fuels from coal and oil shale should be investigated for use with current and future engines. Some believed that efforts should be directed toward producing fuels that are essentially identical to the gasolines and diesel fuels in use today. Others thought there was considerable merit in trying to use less refined fuels and that broad-boiling-range fuels should be investigated for use in stratified-charge engines, Stirling engines, and gas turbines. The fuel properties of greatest concern were the sulfur, nitrogen, and aromatics contents.

Many of the respondents believe that spark-ignition and diesel engines will continue as the major automotive power plants through the end of the century, with their fuel needs dictating the kinds of oil-shale- and coal-derived fuels that might be used. They also believe that engine with less stringent fuel requirements (e.g., the Stirling engine and gas turbine) will not see much use prior to the 1990s.

NATIONAL RESEARCH COUNCIL

ASSEMBLY OF ENGINEERING

2101 Constitution Avenue Washington, D. C. 20418

October 28, 1977

Dear Sirs:

At the request of the Department of Energy (formerly ERDA) the National Research Council has formed an ad hoc panel to investigate the research and development needs related to the refining of synthetic crude oils obtained from coal and oil shale. The specific objective of the ad hoc panel and the current composition of the panel are given in the attachments to this letter.

The panel, in reviewing its assignment, has recognized that potentially significant energy and presumably economic savings are possible if future transportation engines can be designed to operate satisfactorily on fuels from coal and oil shale that do not have to be refined to the same extent as current fuels from petroleum.

The major product output from the refinery will be liquid fuel for transportation. To ensure that the refinery is properly designed to support the optimum fuel/engine combinations, anticipating engine changes that could use less well refined fuel that will be in use about 2000 A.D., the panel has decided to ask experts about their opinions on the quality of fuels that will be required for the kinds of engines expected to be in use by then. Considering your background and experience regarding the matching of automotive fuels and engines, would you please project the fuel specifications that you believe will be required for the engines that will power our land-based transportation systems by 2000 A.D. These engines include: spark ignition; diesel; stratified charge; gas turbine; Stirling; and any other engines.

In looking at fuel quality projections, the following should be considered: distillation characteristics; vapor pressure; impurities (sulfur, nitrogen, ash) content; aromatic content; octane and/or cetane quality. This is obviously not an all-inclusive list, and you should include any other fuel properties that you believe will be important.

your expected changes in fuel properties to those of current specifications (ASTM or other) for the fuels involved.

I would appreciate it if we could receive your response by November 18, 1977. This would give the panel a chance to review and summarize the responses prior to its meeting in early December. I recognize that we are asking you to spend some time essentially peering into your crystal ball. However, I expect that it will turn out to be time well spent if we can get our nation started on the right track toward generating the best fuels for transportation's use in the next century.

Thank you for your cooperation.

Sincerely yours,

John O. Berga
Executive Director

JOB/vs
Attachments

Attachment to letter:

STATEMENT OF TASK

Panel on R&D Needs in Refining Coal and Shale Liquids

The objective of this contract is to define the research and development needs in refining coal and shale liquids to a product slate emphasizing transportation fuels and other distillable fuels.

Survey the program currently underway on processing techniques applicable to coal and shale upgrading. Programs are currently supported by ERDA, Department of Defense, the Electric Power Research Institute (EPRI) and industry.

With the results of the above, define the areas in coal and shale liquids refining and upgrading where research would be desirable from a benefit to cost standpoint and from the standpoint of national needs.

and low emission potential.

- Fuel corrosivity (from chemically active oxygen, sulfur, or nitrogen compounds or compounds that take up water) must be controlled.

- Sulfur, nitrogen, and particulate precursors will need to be controlled because of environmental considerations.

- The metals contents of high-boiling-point fuels must be minimized.

- Crudes from oil shale and coal are likely to contain more troublesome components than petroleum crudes and will very likely require a greater degree of refinery processing.

- Conventional engines of the future (spark ignition and diesel) will require fuels with much the same characteristics as those of current fuels (gasoline and diesel fuel).

- Engines that tolerate fuels of a wider distillation range (e.g., the stratified-charge engine, gas turbine, and Stirling engine) provide greater flexibility in refinery processing.

- It is difficult to forecast engine developments that will permit efficient operation with low emissions on less refined fuels.

Petroleum Company B

- The homogeneous-charge Otto-cycle spark-ignition engine is likely to remain in use for ground transportation until beyond the year 2000. Possible changes in its (gasoline) fuel requirements include (a) a lower Reid vapor pressure, (b) higher 10 and 20 percent evaporated temperatures, and (c) control of the aromatic content. No changes are anticipated in the octane quality, stability, or impurities contents (sulfur, nitrogen, polynuclear aromatics).

- The diesel engine will find increasing use in passenger cars and light-duty trucks through 2000 and will continue to be the engine used most in medium and heavy trucks. Possible changes in diesel fuel specifications include (a) an increase in 90 percent and end-point distillation temperatures (especially if gasoline demand decreases and heavy gas oil is not needed for cracking), (b) a decrease in cetane quality for truck engines if spark-ignition diesel engines come into use, (c) an increase in cetane quality (above 45) for passenger car diesel

matics). The stability cannot deteriorate.

- Prechamber (jet-ignited) stratified-charge engines are not likely to find wide application. If used, they will not permit appreciable changes in present gasolines.

- Open-chamber stratified-charge engines may find application. Throttled engines (Ford PROCO) require a fuel similar to current unleaded gasoline; unthrottled engines (e.g., Texaco TCCS) can use either current fuels or a wide range of other fuels without regard to octane or cetane quality. Volatility is not a major concern. Fuel stability and sulfur, nitrogen, and polynuclear aromatic contents will have to be controlled.

- It is very doubtful if either the gas turbine or Stirling engine will find widespread use by 2000. However, either would permit the use of fuels with few specification restrictions.

Automobile Company A

- It is more energy efficient to refine fuel carefully to achieve best engine performance than to attempt to operate with less refined fuels. This applies to gasoline, diesel, and gas turbine engines likely to be in use by 2000.

- Emphasis should be placed on developing the technology needed to refine coal and shale oil into gasoline and diesel fuels that meet the current specifications for these fuels. Refining efforts should concentrate on reducing sulfur and nitrogen contents to acceptable levels.

- Engines may have to be modified to permit the use of fuels from coal and oil shale, particularly because of their high aromatic contents.

Automobile Company B

- The spark-ignition engine will be the principal engine for passenger cars through the year 2000.

- Stratified-charge engines may come into use eventually. The PROCO engine has significant octane requirements, even though it can tolerate variations in fuel volatility and stoichiometry. The TCCS (Texaco) engine has even greater volatility tolerance and presumably no octane requirements.

- To make diesel engines more desirable for passenger car use, starting performance may have to be improved by using lower compression

However, for reasons of customer convenience, supply, and logistics, it is likely that these engines will be designed to use gasoline.

Automobile Company C

- In the future, engines may be able to tolerate less volatile fuels with higher concentrations of sulfur, nitrogen, and aromatics, provided emissions can be held at acceptable levels. Emission constraints may become the main factor in determining the extent to which fuel properties can be relaxed.

- Major changes in engine efficiencies are not anticipated for the fuel changes considered possible.

- The engines of the future, in order of decreasing likelihood, are the homogeneous-charge spark-ignition, diesel, stratified-charge, gas turbine, Stirling, and Rankine engines. The engines fall in the same order when listed according to their increasing tolerance to variations in fuel specifications.

- In evaluating future fuel-engine matches, the following factors must be considered: combustion, performance, cost, durability, emissions, safety, convenience, and fuel and resource consumption.

- Spark-ignition engines will require volatility and octane quality similar to that of current gasoline. Fuel-injected spark-ignition engines may have less stringent volatility requirements than carbureted engines. They might also tolerate more viscous fuels if octane quality is not compromised.

- Diesel engines could probably tolerate less volatile fuels if emissions of particulates, smoke, hydrocarbons, and odor were acceptable. Higher sulfur, nitrogen, and ash contents may not be acceptable because of emission and engine durability problems, however.

- Cetane quality should remain at or near current levels.

- The PROCO-type direct-injection stratified-charge engine requires a fuel similar to the unleaded gasoline now available. The Texaco-type engine has less stringent fuel requirements, particularly for octane quality; its fuel requirements resemble those of diesel engines (except for cetane quality).

- The open-cycle gas turbine engine has a wide fuel tolerance, the most stringent requirement being that the fuel flow adequately at the lowest temperature encountered in service. Fuels with high aromatic con-

• External combustion engines (e.g., Stirling, Rankine, and closed cycle gas turbines) should be able to burn any liquid hydrocarbon fuel that can be pumped at the lowest service temperature and still meet environmental and engine life constraints.

• Special concern should be given to distillate fuels for railroad diesel engines that are designed for ASTM 2D fuel. This type of fuel must remain available for as long as these engines are in operation, which may be 20 years or longer. Future railroad diesels could be designed to use ASTM 4D fuel, if environmental constraints can be met.

Automobile Company D

• There is no clear indication of the benefits in process cost and energy savings that can result from reducing fuel properties in terms of cetane, octane, distillation ranges, freedom from impurities, and so on.

• For today's diesel engines, the most desirable fuels are the ones with the highest cetane quality, minimum sulfur, minimum aromatics, etc. For gasoline engines, the most desirable fuels are the ones with the highest octane, minimum octane improving additives, etc. Engines have useful lives of 10-20 years, especially in industrial and agricultural applications. Thus, fuels similar to current fuels will have to be sold until the year 2000, since no major changes in engines are anticipated, at least through the early 1980s.

• Some stratified-charge, gas turbine, and Stirling engines do not have octane or cetane requirements. However, fuels for these engines will need to remain liquid at normal ambient temperatures (-30°F to 120°F) and be seasonally blended. These engines cannot tolerate fuel impurities that could cause corrosion or unacceptable levels of exhaust pollutants. If unacceptable hydrocarbon pollutants are not generated (even in small quantities), however, higher aromatic levels can probably be tolerated.

Independent Research Laboratory A[a]

• Distillation characteristics of fuels for Stirling and gas turbine engines can vary from those of gasoline to those of No. 2 diesel fuel. A broad-cut fuel could be used. An open question is whether these engines can tolerate tank-to-tank variations in distillation characteristics.

• Vapor pressure restrictions required by evaporative and refueling emission standards could restrict the light-end content of all fuels.

the lean operating Stirling and gas turbine engines are likely to oxidize all fuel sulfur to SO_2 or sulfates. Ash content will need to be controlled to lessen engine wear and particulate emissions. Trace metals such as vanadium may also need to be controlled.

- Control of the aromatic content will make it possible to reduce carcinogenic emissions.

Independent Research Laboratory B

- With the decline in the supply of petroleum fuels forecast for the near future, the following sequence of events is expected to occur:

1. The introduction of conventional engines that are less sensitive to fuel quality (e.g., stratified-charge engines and engines with closed-loop systems)

2. The introduction of hybrid fuels (alcohol-gasoline blends, carbonaceous diesel fuels)

3. The introduction of other engines (e.g., gas turbines)

4. The end of 100 percent petroleum fuels

5. The introduction of either unconventional engines (e.g., external combustion types) or unconventional fuels (e.g., nonpetroleum compositions)

6. The introduction of unconventional engine-fuel systems (e.g., an external combustion engine and frangible solid fuels).

- From 1985 to 2000, the fuels used for highway transportation are likely to be gasoline, diesel fuel, broad-cut fuel, gasoline-alcohol blends, and carbonaceous hydrocarbon slurries. These fuels will be obtained primarily from petroleum with inputs from coal, oil shale, and biomass.

- From 1990 to beyond 2000, the transportation fuels are likely to be solids, gels, and slurries or emulsions obtained from coal, oil shale, and biomass. Pure and mixed alcohols and pure synthetic liquid hydrocarbons from these sources are doubtful. Hydrogen, methanol, and ammonia are all unlikely fuels.

- There will probably be two octane grades of unleaded gasoline in use in the year 2000. Metallo-organic antiknock agents will probably not

• Both 1-D and 2-D diesel fuels are likely to survive beyond 2000. A broad-cut fuel may become an alternative to 1-D fuel, however. Fuel stability may require tighter control.

• Broad-cut fuels may come into use because they can reduce refinery energy losses and increase refinery yields; they can reduce refinery energy losses because energy does not have to be expended to increase either octane or cetane quality. Broad-cut fuels can be used in some stratified-charge and gas turbine engines and may also find use in future diesel engines.

• Mid-distillate hydrocarbons containing up to 20 percent suspended carbonaceous particles would be attractive fuels for use in diesel, gas turbine, stratified-charge, and Stirling engines. The carbonaceous particles would be obtained by pulverizing the products from the solvent refining of coal. Research must be done to prove the fuels which offer the best cost-energy potential.

BIBLIOGRAPHY

Bailie, J. D., G. W. Michalski, and G. H. Unzelman. 1978. MMT [methyl-cyclopentadienyl manganese tricarbonyl]: A Versatile Antiknock. Paper presented at annual meeting of National Petroleum Refiners Association, San Antonio, Tex., March 19-21. Prepared for Ethyl Corporation. (Available from National Petroleum Refiners Association, Suite 1000, 1899 L Street NW, Washington, D.C. 20036, $2. AM-78-36).

Duffy, M. 1977. Motor Fuel Consumption--The Automotive Market and State Revenue. In Proceedings of the 51st Annual Meeting of the North American Gasoline Tax Conference, San Antonio, Tex., November 13. (Available from North American Gasoline Tax Conference, 444 N. Capitol Street, Washington, D. C. 20001.)

E. I. du Pont de Nemours & Company. 1977. Factors Affecting the Future of Gasoline. Du Pont 1977 Technical Conference. p. A-1. Petroleum Chemicals Division. Wilmington, Del.

Executive Office of the President. 1977. The National Energy Plan. Office of Energy Policy and Planning. Washington, D.C.: Government Printing Office.

Lange, D. 1977. Refiners Seen Ready for Record Gasoline Binge. Oil and Gas Journal 75(21):19-21.

ll, J. P. 1978. Alternative Fuels and Combustion Problems. lternative Hydrocarbon Fuels: Combustion and Chemical Kinetics, C. T. Bowman and J. Birkeland. Progress in Astronautics and nautics Series, Vol. 62, pp. 3-20. Cambridge, Mass.: MIT Press.

al Aeronautics and Space Administration. 1976. Minutes of June meeting of Ad Hoc Panel on Jet Engine Hydrocarbon Fuels, NASA arch and Technology Advisory Council Committee on Aeronautical ulsion, Lewis Research Center, Cleveland, Ohio.

____. 1977. NASA Workshop on Jet Aircraft Hydrocarbon Fuels. . Washington, D.C.: National Aeronautics and Space Administration ference Publication 2033).

d Gas Journal. 1977a. Gasoline Decontrol Proposed for November 1. 3):32-33.

____. 1977b. Exxon Fine Tunes U.S. Energy Forecast. 75(52):32-

on, R. M., and G. G. Pollack. 1977. Gasoline Consumption for the Fleet of Tomorrow. Standard Oil Company of California. Warren-, Pa.: Society of Automotive Engineers (SAE Paper 770670).

eum Economist. 1977. United States: Looking Ahead to 1990. 2):483-484.

r, H. A., and T. O. Wagner. 1977. Economics of Manufacturing Auto-ve Diesel Fuel. 1977 Proceedings--Refining Department, Vol. 56, 87-91. Washington, D. C.: American Petroleum Institute.

4 COAL LIQUEFACTION PROCESSES

There are both direct and indirect routes for the conversion of coal to high-quality transportation fuels. In the indirect routes, the molecular structure of the coal is completely destroyed and the simple molecules of CO and H_2 that result are used to build molecules of combustible liquids. In the direct routes, the coal molecules are broken down into lower boiling hydrocarbons while preserving as many as possible of the original chemical bonds in the coal.

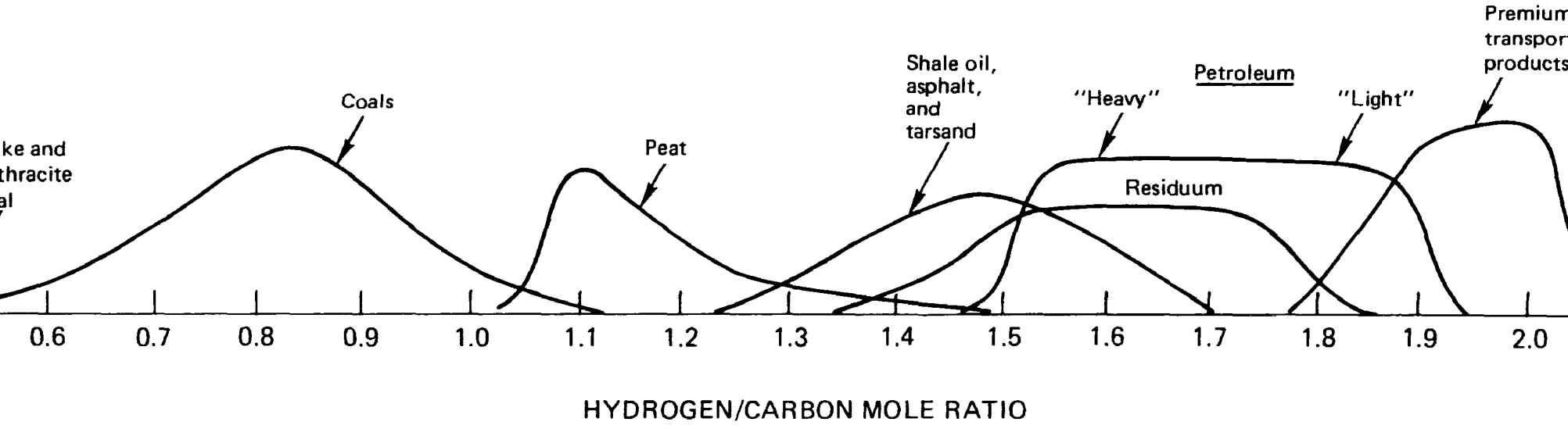
The products of the two routes have different refining characteristics. The liquids from the direct processes resemble petroleum crudes and can be refined in much the same way into high-quality transportation fuels. The liquids from the indirect processes vary from process to process and differ in character.

This chapter deals primarily with the refining of coal liquids obtained by direct routes. The refining of coal liquids obtained by indirect routes is discussed only when it can add perspective to some aspect of the overall problem.

THE ROLE OF HYDROGEN

Central to any discussion of the conversion of coal to liquids and ultimately to high-quality transportation fuels is the important role of hydrogen. Hydrogen is required not only to increase the hydrogen/carbon (H/C) ratio from that available in coal to that required in the end-products, but also to remove the undesirable heteroatoms (N, S, and O) present in the coal molecules.

The problem with the H/C ratios of coal products can be seen in Figure 5. In refining petroleum crudes, the most common method of increasing the H/C ratio is to reject carbon as a low-hydrogen coke or residuum (Figure 5). This practice plays a varying role in coal conversion processes. In some processes (such as pyrolysis), a liquid with a higher H/C ratio is produced for further refining, and a char with



igure 5 Hydrogen/carbon ratios for various hydrocarbon sources and end products (Whitehurst, 1978)

Processes currently in use for hydrogen production ultimately involve the reaction of steam with carbon, either directly or as carbo monoxide or a hydrocarbon. These processes, described in Chapter 7, are both costly and energy inefficient. Thus, increasing the efficien with which hydrogen is used in the liquefaction and refining processes is critical to reducing the overall cost of converting coal to transportation fuels.

COAL PYROLYSIS

Pyrolysis processes that operate at high temperatures are able to convert about a third of the coal feedstock to liquids and gases that have higher H/C ratios than the original coal, carbon being removed in chars that have lower H/C ratios.

The Char Oil Energy Development (COED) process (Jones, 1975) is a typical example. In this process, coal is pyrolyzed in a series of fluidized beds, with the temperature increasing from bed to bed. In the operation of the COED pilot plant diagramed in Figure 6, bed temperatures were 500°F, 850°F, 1000°F, and 1650°F, the temperature being increased by the addition of oxygen.

The properties of typical products of the pyrolysis of Pittsburgh No. 8 coal are shown in Table 8. The figures indicate that the addition of a large amount of hydrogen would still be required to increase the H/C ratio to that of premium transportation fuels and remove the remaining heteroatoms. It should be noted that the gas produced had a overall H/C ratio of 10.9 because of the large quantities of hydrogen and methane that resulted. This represents a loss of valuable hydroge that could have gone toward increasing the H/C ratio of the liquid. The liquid had an API gravity of -5°, a pour point of 100°F, and a viscosity of 70 centipoises at 210°F; its physical and distillation prope ties resemble those of a petroleum crude somewhat, but it has a much lower H/C ratio. (See Figure 7). The high nitrogen content of this liquid would present refining problems.

The char from this process could be used as a boiler fuel but wou be high in sulfur if a high-sulfur coal were used as the feedstock. T char could also be gasified and the syngas used as a fuel gas, convert to hydrogen by the shift reaction, or converted to liquid fuels by one of the indirect conversion processes.

Pyrolysis carried out in a hydrogen atmosphere (hydropyrolysis or hydrocarbonization) could improve the liquid yield, thereby improving product quality and reducing the sulfur content of the liquid product

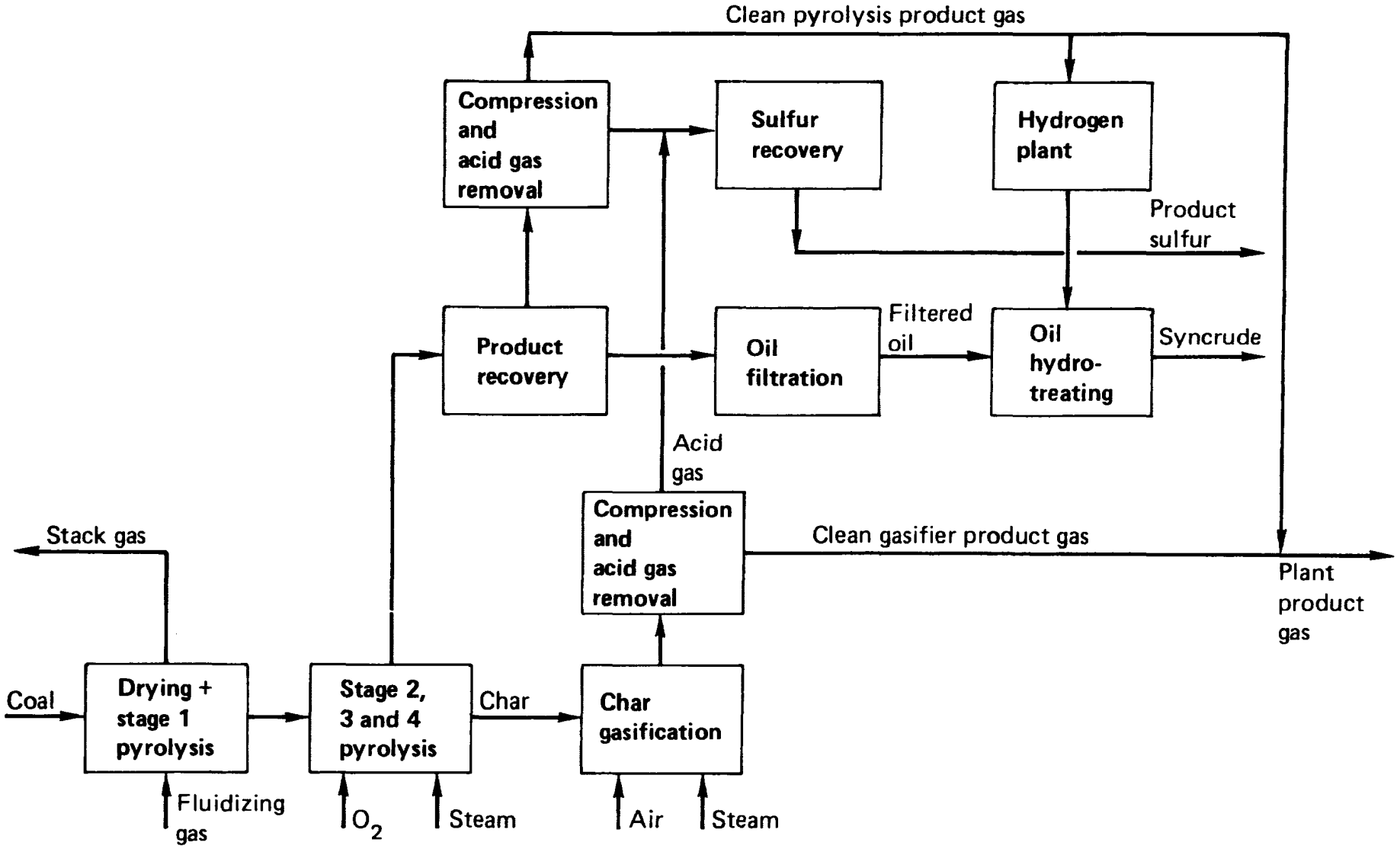
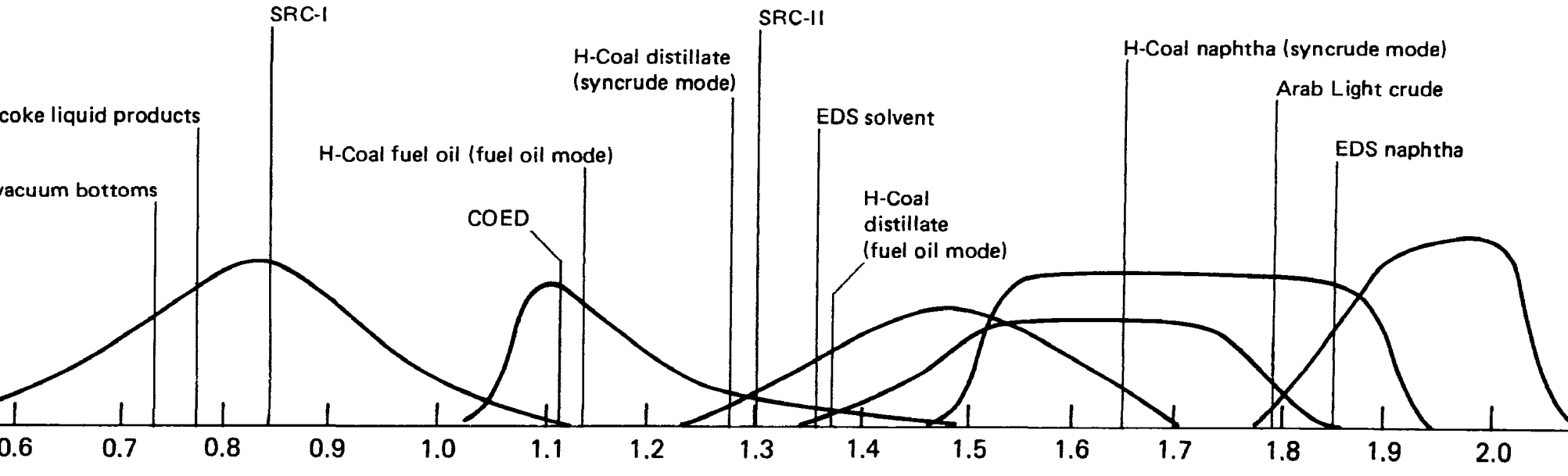


Figure 6 COED coal liquefaction process, with char gasification (Jones, 1975)

Table 8 Properties of coal feed and products from COED pyrolysis (Pittsburgh No. 8 coal)

	Coal	Oil	Char	Pyrolysis gas
Yield	--	0.85 barrel per ton	1,266 pounds per ton	3,675 standard cu feet per ton
Hydrogen/carbon ratio	0.83	1.12	0.31	10.9
Composition, wt %				
Carbon	76.2	82.68	76.9	--
Hydrogen	5.3	7.73	2.0	23.75
Oxygen	6.7	2.2	1.9	--
Nitrogen	1.4	6.50	1.2	--
Sulfur	3.8	0.85	4.3	--
Ash	6.6	0.04	13.9	--
Carbon monoxide	--	--	--	29.50
Methane	--	--	--	38.26
C_2+ gas	--	--	--	8.49
Pyrolysis oil				
Gravity, ^{o}API at 60^{o}		-5		
Pour point, ^{o}F		100		
Viscosity, centipoises at 210^{o}F		70		
Distillation temperatures, ^{o}F				
Initial boiling point		385		
5%		415		
10%		460		
20%		550		
30%		630		
40%		730		
50%		795		
60%		860		
End point		905		
Recovered, percent		70		
Residual, percent		30		



ure 7 Hydrogen/carbon ratios for products of coal liquefaction pilot plants, with Arab Light crude for comparison (adapted from Whitehurst, 1978)

SOLVENT PROCESSES WITHOUT THE ADDITION OF CATALYSTS

If an appropriate fraction of the liquid product obtained from the hea ing of coal is returned to the reaction zone, it improves the conversi of the coal to a liquid by acting as a solvent and also by aiding the shift of hydrogen and the rearrangement of chemical bonds within the coal molecule. In most of the processes making use of these effects, high-pressure hydrogen atmosphere is maintained in the reactor in whic the coal is dissolved.

In Solvent-Refined Coal (SRC-I and SRC-II) processes (Sullivan et al., 1979; Synthetic Fuels, 1979), the temperature in the dissolvi vessel is maintained at about 850°F and the pressure at 1000-1500 psi, depending on the particular coal and process used, with the required hydrogen provided from an outside supply. By returning part of the liquid produced to the dissolving vessel, the coal is converted to a product that is fluid at the temperature in the vessel. The time required varies from a few minutes to about an hour, depending on the particular process and the product characteristics required.

In the SRC-I process shown in Figure 8, the solvent is taken fro the vacuum distillate fraction boiling below 1000°F. Contact times are about 30-60 minutes. Although the H/C ratio of the product (Table 9) does not differ very much from that of the coal used, considerable hydrogen is consumed (Table 10), the quantity equaling that in the gas produced. The ash is removed from the product by filtration or solve precipitation. Table 9 shows the physical and chemical characteristi of a typical SRC-I product (solid at room temperatures), and Table 10 shows typical yields. To be upgraded, this product must be hydrogenated further.

When the contact time in the SRC-I process is reduced to about 5 minutes, the H/C ratio in the product remains about the same as that the coal feedstock, but the hydrogen consumption and gas production a lowered. If this product were then de-ashed and hydrogenated in a separate ebullating-bed reactor (e.g., an LC-Fining or H-Oil reactor) the net result would be a good syncrude and an overall reduction in hydrogen consumption (Kleinpeter et al., 1979; Longanbach et al., 197 Schindler, 1980).

In the SRC-II process (Figure 9), the dissolving conditions are severe; temperatures and pressures are higher, and contact times are longer. The solvent is a portion of the slurry bottoms rather than a distillate product as in SRC-I, and the product is sufficiently volat to be removed by vacuum distillation. The product is liquid at room

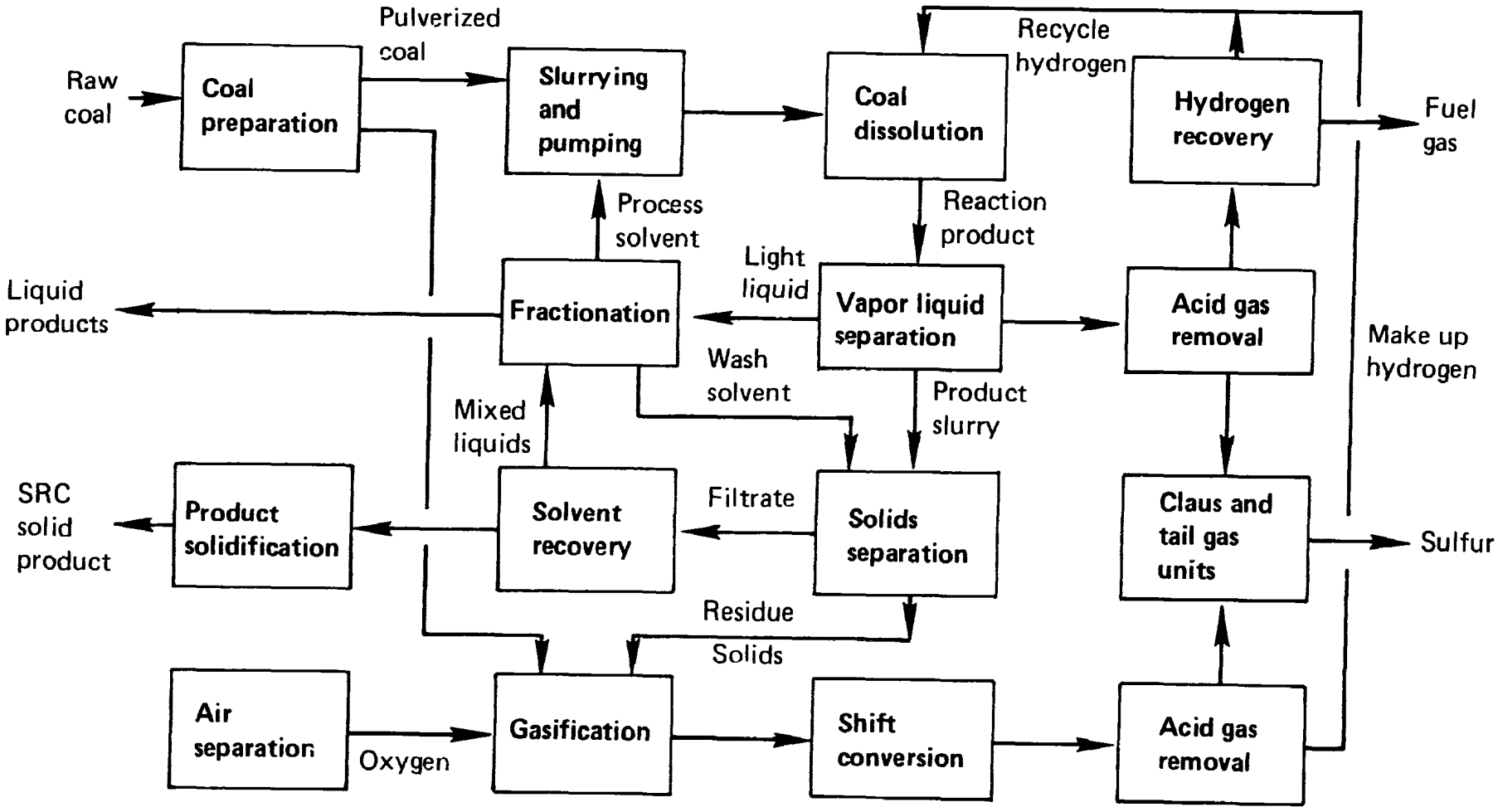


Figure 8 SRC-I process, without the addition of catalysts (Sullivan et al., 1979; Synthetic Fuels, 1979)

	SRC-I	SRC-II
Gravity, °API	-14.6	18.6
Hydrogen/carbon ratio	0.85	1.3
Composition		
Hydrogen, wt %	6.1	9.1
Oxygen, wt %	4.5	3.8
Nitrogen, wt %	2.0	0.85
Sulfur, wt %	0.9	0.3
Ash, wt %	0.22	0.004
Aromatic carbon, wt %	81	58
Chloride, parts per million	50	50
Nominal boiling range, °F	900+	160-800
Distillation temperatures, °F		
Initial boiling point	159	56
5%	943	189
10%	1017	241
30%	1161	379
50%		424
70%		473
90%		562
95%		642
End point		820
Hydrogen consumption, standard cubic feet per ton	7,400	15,500

Source: Sullivan et al. (1979).

has been greatly decreased over that of SRC-I as a comparison of the two distillate curves in Table 9 shows. The hydrogen to carbon ratio is now 1.3 as shown in Table 9 and Figure 9. Table 10 gives typical yields from this process. Although the boiling range of SRC-II liqui is good for high quality fuel production, the hydrogen to carbon rati is still a long way from that required for high quality transportatio fuels. Some properties of an Arab Light crude are given in Table 11

Table 10 Hydrogen consumption and hydrocarbon yields from various coal liquefaction processes

	SRC I (Illinois No. 6)	SRC I (Kentucky No. 9)	SRC II (Kentucky No. 9)	EDS (Illinois No. 6)	H-Coal (Illinois No. Fuel oil	Sync
Hydrogen consumed, standard cubic feet per ton of coal[a]	6,700	7,400	15,500	14,600	13,400	18,
Process yields, based on coal						
Light gases, pounds per ton of coal						
CH_4	42.6	50.7	116.8	65.6	45.7	51
C_2-C_3	52.7	62.7	163.2	102.2	91.4	103
Liquid hydrocarbons, barrels per ton of coal						
C_4-380°F	0.26	0.44	0.96	1.53	0.75	1
380-650°F	0.35	0.30	1.07	0.21	0.71	0
650-1000°F	0.70	0.16	0.20	0.32	0.72	0
1000°F+ (SRC)	2.17	2.47	1.11	1.32[b]	1.21[c]	0
Total C_4+ liquids	3.48	3.37	3.34	3.38	3.39	3
C_4-1000°F liquid, vol %	37.6	26.7	66.7	60.9	64.3	79
Hydrogen consumed per C_4-1000°F liquid, standard cubic feet per barrel	5,100	8,200	7,000	7,100	6,100	6,
Ratio of CH_4 to H_2 consumption, pounds per million standard cubic feet	6.3	6.8	7.5	4.5	3.4	2
Ratio of CH_4 to C_4-1000°F liquid, pounds per barrel	32.5	56.3	52.4	31.8	20.9	17

[a]As received. Hydrogen externally supplied.

[b]Assumed unconverted coal, 8.2 weight percent of coal. Product coked and coke gasified to produce either hydrogen or fuel gas.

[c]Product gasified to produce hydrogen.

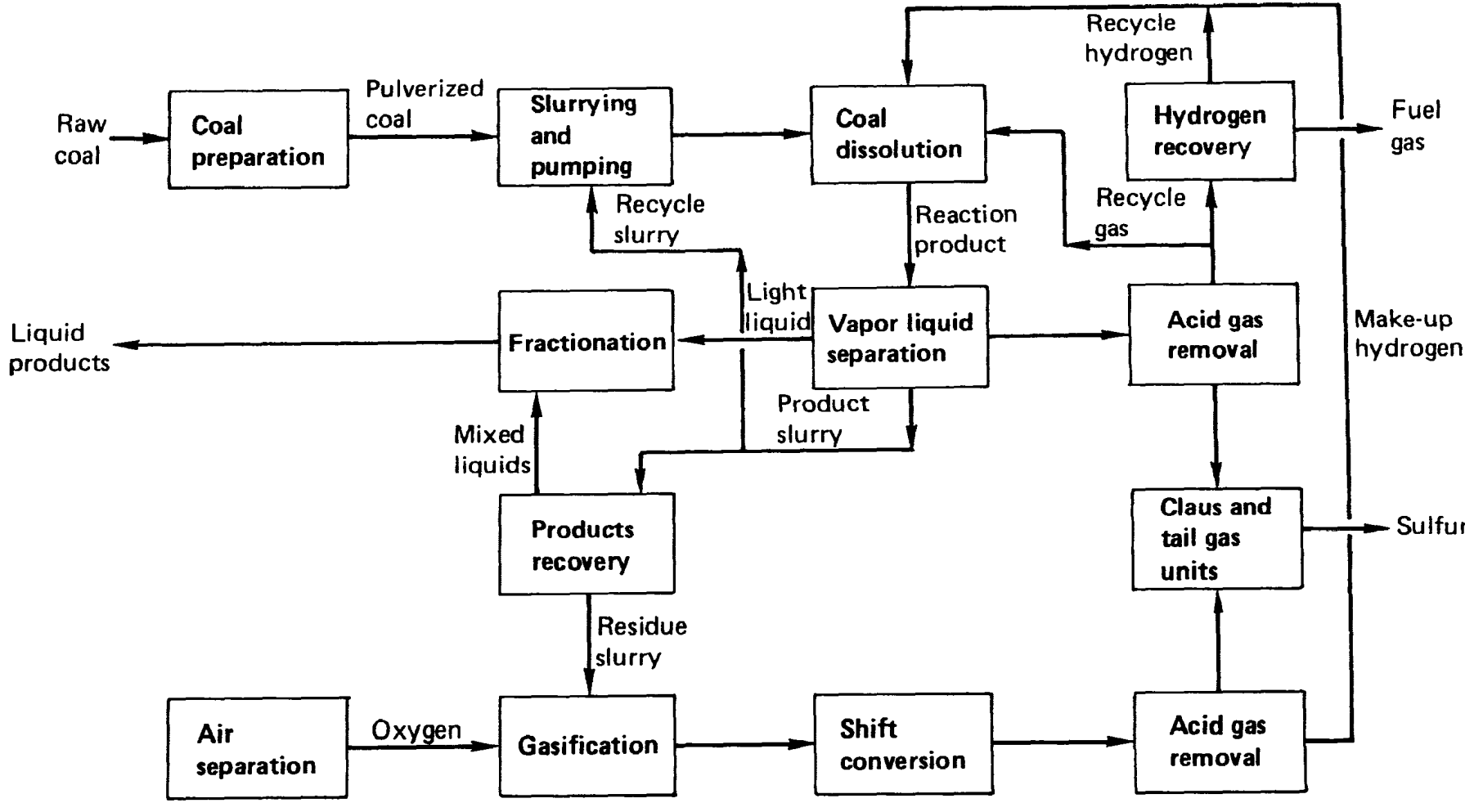


Figure 9 SRC-II process, with catalysts (Sullivan et al., 1979; Synthetic Fuels, 19

Gravity, °API	34.7
Hydrogen/carbon ratio	1.79
Composition	
Hydrogen, wt %	12.8
Oxygen, ppm	40
Nitrogen, ppm	770
Sulfur, wt %	1.70
Aromatic carbon, wt %	13
Distillation fractions, wt %	
Naphtha, C_5-400°F	26.6
Atmospheric gas oil, 400-650°F	24.9
Vacuum gas oil, 650-1000°F	27.9
Vacuum residue, 1000°F	20.6
Total	100.0

In the past, solvent-refining processes like SRC-I and SRC-II were thought to be noncatalytic, but recent work has shown that the ash of the coal has a degree of catalytic activity that plays an important role in the liquefaction process. The catalytic activity of the ash varies from coal to coal.

SOLVENT PROCESSES INVOLVING THE ADDITION OF CATALYSTS

Although some coal liquefaction processes rely on the catalytic activity of the coal ash alone, this activity is weak. In many of the coal liquefaction processes developed, additional catalytic material is added from an external source.

External catalytic material is generally supplied in one of two ways: (a) by adding the catalyst to the reactor in which the solvent is being hydrogenated prior to its transfer to the coal liquefaction reactor, as in the Exxon Donor Solvent process (Fant, 1978; Epperly, 1978, 1979) or (b) by adding the catalyst to the coal in the liquefaction reactor in the presence of hydrogen, as in the H-Coal process (Stein

Figure 10 is the flow diagram from a design study made for a commercial EDS plant. The solvent (a 400-850°F boiling range material) is hydrogenated in the presence of a catalyst and then mixed with the coal to form a slurry that is fed to a liquefaction reactor maintained at a temperature of 800-850°F and a pressure of 1500-2000 psi.

The only catalyst present in the liquefaction reactor is that which is naturally present in the coal ash. The product of this reactor is a slurry of solvent, liquefaction products, unconverted coal, and ash that is then separated by distillation into gas, naphtha, distillates, and a vacuum bottom slurry. The latter is fed to a flexicoker, which contains a coking and gasifying unit. If syngas were produced in the gasifier, it could be used to make hydrogen. In the design shown here, the gasifier produces fuel gas, and the hydrogen required is obtained by the steam reforming of the gas from the distillation unit.

Much of the information for this design was developed from the recycle coal liquefaction unit shown in Figure 11. The properties of its major products (A, B, and C) are given in Table 12. The naphtha stream, with an H/C ratio of 1.85 and a hydrogen content of 13.32 percent by weight, is within the range required for high-grade transportation fuels (Figure 7). However, examination of the flow diagram of the proposed plant, shown in Figure 10, suggests that the naphtha fraction produced should contain less hydrogen than is obtained from the pilot unit, since some of the streams in the commercial plant receive less hydrogenation than the product from the pilot plant. The 1.36 H/C ratio of the 400-700°F solvent of Table 12 also indicates that some further hydrogenation will be required to bring its H/C ratio up to the range of conventional petroleum-derived fuels.

As can be seen from the table, the solvent is highly aromatic and will need to be hydrogenated considerably to produce diesel and jet fuels. Distillate fuels become highly naphthenic after hydrogenation, however, and naphthenic diesel and jet fuels have combustion qualities that may leave much to be desired.

The combined distillate streams from the liquefaction unit, solvent hydrogenation unit, and coker of the commercial EDS plant design of Figure 10 will have a lower H/C ratio and higher aromatic content than the hydrogenated solvent of the recycle unit of Figure 11 (Table 12), because of the differences in the extent of hydrogenation between the two flow schemes. Figure 7 shows how the EDS products compare with the products of other processes. This figure also shows the hydrogen/carbon ratio of the liquid products from a typical coker pilot run with vacuum bottoms.

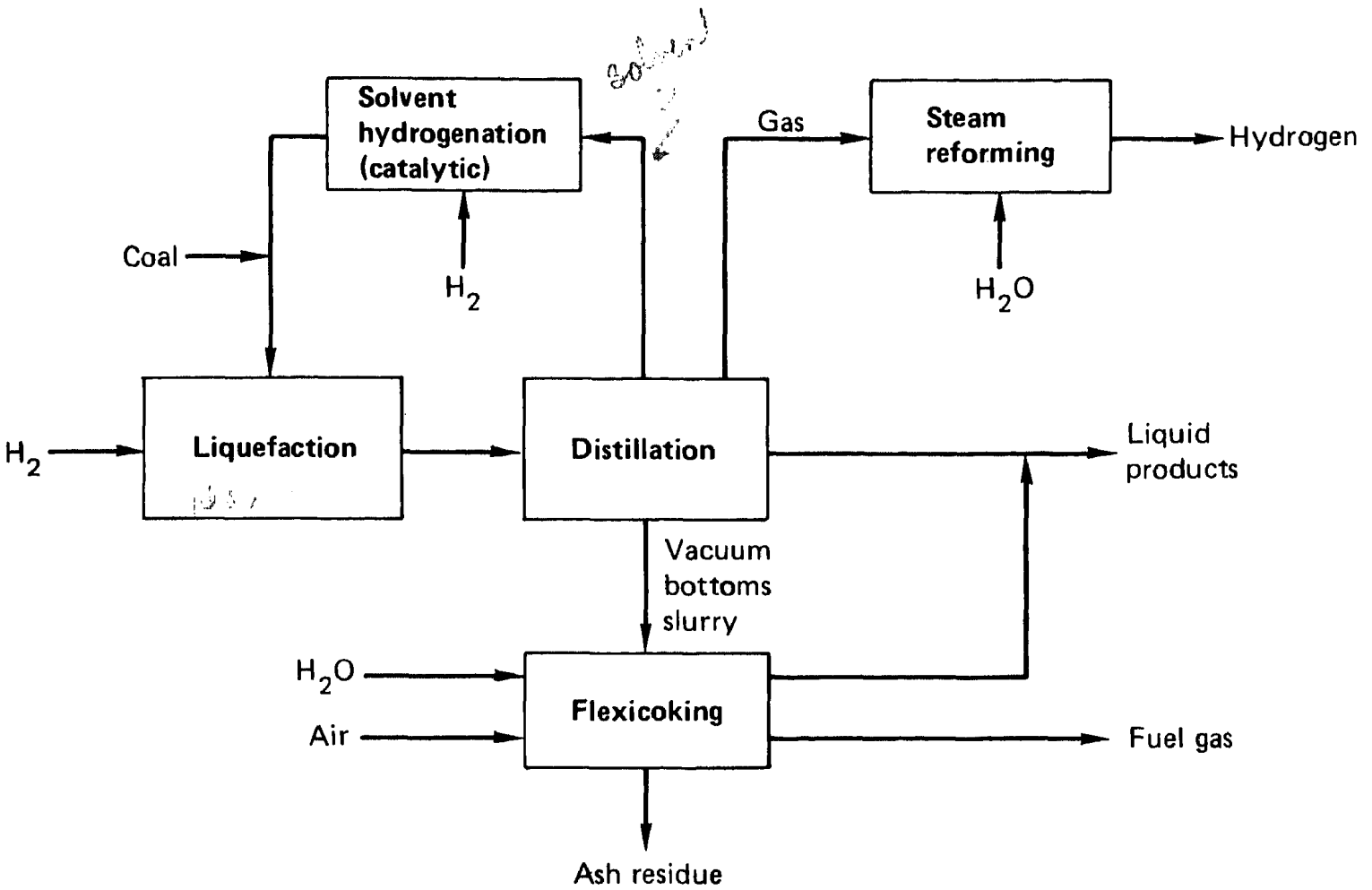


Figure 10 Flow design of commercial coal liquefaction plant based on Exxon Donor Solvent process

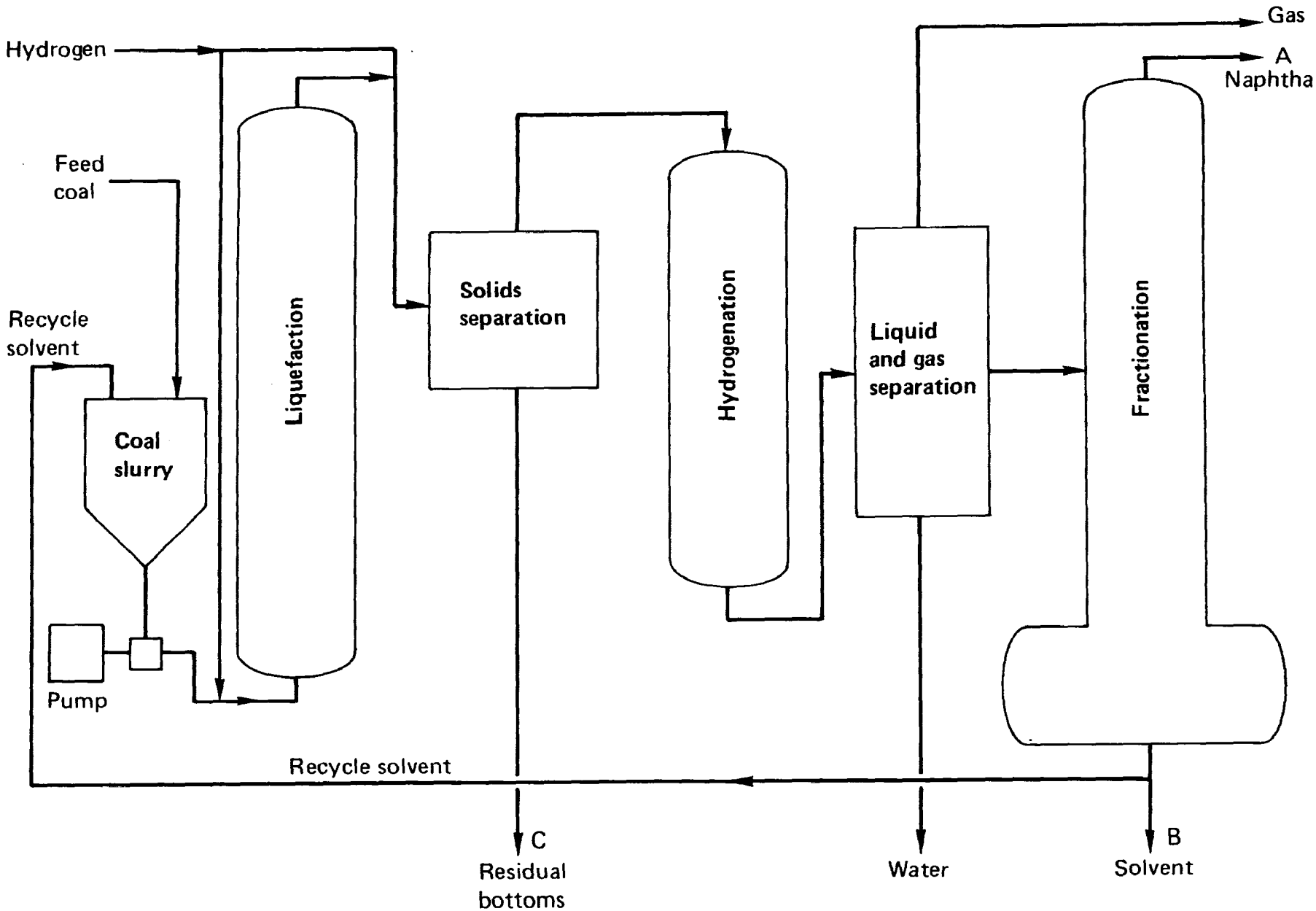


Figure 11 Recycle coal liquefaction process (Epperly, 1979)

	Coal (dry basis)	Naphtha C_5-400°F (A)	Solvent 400-700°F (B)	Residual Bottoms (C)
Gravity, °API		42.1	15.7	--
Hydrogen/carbon ratio	0.89	1.85	1.36	0.74
Composition, wt %				
Hydrogen	4.98	13.32	10.18	4.22
Sulfur	4.39	0.012	0.004	2.18
Nitrogen	11.15	0.01	0.04	1.36
Oxygen	15.89	0.46	0.22	12.46
Ash	12.00	--	--	20.61
Aromatic carbon	--	19	53	--
Distillation temperatures, °F				
5%		158	397	89% 1000°F+
15%		206	407	
25%		226	434	
50%		310	501	
75%		362	582	
95%		382	727	

Source: Epperly (1978).

H-Coal Process

In the H-Coal process, the catalyst is added directly to the mixture of coal and solvent, so that the solvent is continuously hydrogenated in the presence of the dissolving coal. A flow diagram of this process is given in Figure 12.

The coal-slurry and hydrogen streams are introduced at the bottom of the ebullating-bed reactor and maintained in a fluidized ebullating state by using a pump to recirculate the liquids. The heat transfer that results from this action keeps the temperature of the reactor contents essentially uniform. The ebullation also aids in handling the solid coal and catalytic material in the reactor. Temperatures of the order of 850°F and pressures up to 3000 psi are used. The products are fractionated, and the vacuum tower bottoms (containing the 950°F+ product

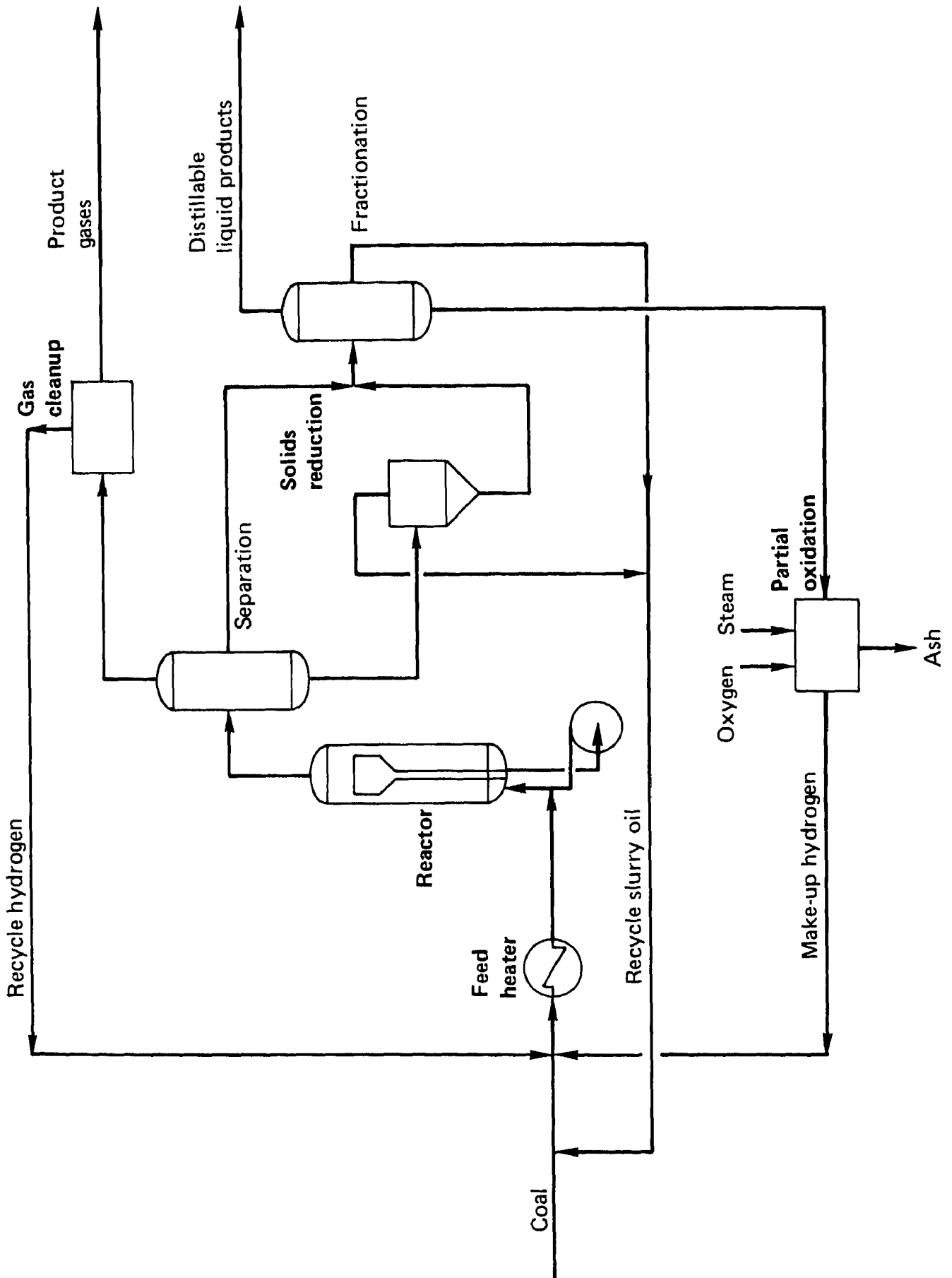


Figure 12 H-Coal liquefaction process (Hydrocarbon Research, 1978)

Two modes of operation are envisioned: a fuel oil mode for the production of boiler fuels, and a syncrude mode to produce material suitable for refining to high quality transportation fuels. The latter is at present considered the more likely for commercial application. The properties and yields of products from the syncrude mode are shown in Table 13; other examples of yields are given in Table 10. Hydrogen/carbon ratios of products of the syncrude mode are approximately 1.28; aromatic carbon analyses show these products to be highly aromatic. Distillation studies show that the syncrude and fuel oil boil at temperatures below 950°F, and contain nothing that corresponds to the residuum of petroleum crude, seen in the Arab Light crude of Table 11. The reason for this is that the higher boiling fraction that corresponds to the residuum is gasified to produce hydrogen for the process. The naphtha from the syncrude mode is highly naphthenic and a good feed for the production of high-octane gasoline in a platinum reformer.

HYDROGEN PRODUCTION AND USE IN DIRECT LIQUEFACTION PROCESSES

In some versions of each of the direct liquefaction processes discussed above, gasification of part of the products (char, vacuum bottoms, etc.) is an essential part of the process, with gas used either as a fuel gas or as a source of hydrogen for the liquefaction and refining processes. In these processes, 30-40 percent of the energy content of the coal is used in the gasifier, with the amount depending on the type of process. When the syngas is used to produce hydrogen to hydrogenate the coal and coal liquefaction products, some of this energy becomes part of the energy of the hydrocarbon fractions, but a substantial energy loss and increase in cost still result.

Table 14 shows the three ways in which the external supply of hydrogen is used in the processes that require it. The added hydrogen (1) hydrogenates the coal and coal products to products containing more than three carbon atoms (C_4+ liquids); (2) produces hydrocarbon gases containing one to three carbon atoms (C_1-C_3 gases); and (3) converts the heteroatoms (S, N, and O) to H_2S, NH_3, and H_2O, permitting their removal from the product.

In Table 14, all the hydrogen in the coal is assumed to end up in the C_4+ liquid. Where a particular atom of hydrogen comes from (the hydrogen gas or the coal) or where it goes (into the gaseous or liquid product) is of course not ascertainable, but this method of accounting is adequate for an overall determination of hydrogen consumption. As seen from the table, essentially no net hydrogen is added to the C_4+ product in the SRC-I process. (In one case, 0.03 pounds per hundred pounds of coal is added, and in the other 0.16 pounds per hundred

	Coal feed (dry basis)	Product[a]
Properties		
Analysis, wt %		
Carbon	70.88	88.29
Hydrogen	4.91	9.43
Oxygen	8.57	1.76
Nitrogen	1.47	0.38
Sulfur	3.47	0.14
Ash	10.61	<0.01
Aromatic carbon	--	55
Hydrogen/carbon ratio	0.83	1.28
Kinematic viscosity at 100°F, cSt	--	4.20
Gravity, °API	--	14.1
Yields, wt % dry coal		
Waste gases		6.01
C_1-C_3 gases		10.63
C_4-C_6 gases		4.12
IBP-400°F Naphtha		14.21
400-650°F Distillates		22.26
650-975°F Distillates		6.48
975°F+ Residual oil		19.00
Unconverted coal		5.78
Ash		11.51
Total		100.00

[a]Properties of 350-975°F product; yields include total product yields.

Source: Stein, et al., 1977, 1978; Johanson and Comolli, 1978.

14 Hydrogen use (on a moisture- and ash-free basis) in various coal liquefaction processes

	SRC I (Illinois No. 6)	SRC I (Kentucky No. 9)	SRC II (Kentucky No. 9)	EDS (Illinois No. 6)	H-Coal (Illinois No.
					Fuel oil
en in coal, pounds per pounds of coal	5.73	5.58	5.58	5.66	5.34
en in C_4+ liquid, pounds 100 pounds	5.76	5.42	6.27	6.91	5.84
en consumed, pounds per pounds of coal	2.2	2.3	5.67	4.61	3.97
drogen consumed by C_4+ id, pounds per 100 ds of hydrogen	0.03	-0.16	0.69	1.25	0.50
en used in heteroatom val, pounds per 100 pounds oal	0.62	0.84	1.45	1.51	1.56
en in C_1-C_3 gases, pounds 100 pounds of coal	1.55	1.62	3.53	1.85	1.91

more goes toward the removal of the heteroatoms in the SRC-II, EDS, and H-Coal processes.

When one examines how the use of hydrogen breaks down on a percentage basis (Table 15), it becomes apparent that a sizable portion of it (32-70 percent) goes into the production of the C_1-C_3 gases. While these gases are valuable products in themselves, they consume a disproportionate amount of relatively expensive hydrogen. Methane, for example, has an H/C ratio of 4, double that of the premium transportation fuels.

The cost of converting coal to transportation fuels could be lowered if the amount of hydrogen consumed in producing the C_1-C_3 gases could be reduced. Short-contact-time experiments on the mechanism of coal liquefaction (Whitehurst et al., 1976, 1977) show that a considerable reduction in gas production is possible.

Another way to reduce the hydrogen requirements of coal conversion processes is to modify end-use equipment to allow the use of fuels with lower H/C ratios. Since such fuels would be highly aromatic, they could be used in spark-ignition engines but might present problems in diesel engines.

DIRECT LIQUEFACTION PROCESSES WITH DECREASED HYDROGEN CONSUMPTION

As pointed out above, a short-contact-time (SCT) version of the SRC-I process can produce SRC liquids with a lower consumption of hydrogen. Lummus is developing a two-stage liquefaction process (Schindler, 1980) in which the product of an SCT unit is de-ashed and passed to an ebullating-bed LC-Fining unit for further conversion. The solvent is obtained from the LC-Fining product and recycled back to the SCT dissolver. Figure 13 is a flow diagram of this process. A comparison of the process' hydrogen consumption (Table 16) with those of other processes (Table 14) shows a substantial improvement.

Reduced hydrogen use has also been achieved in the Lummus Clean Fuels from Coal (CFFC) process (Long et al., 1979) by using a series of plug-flow expanded-bed reactors without any internal recycling (instead of continuous stirred-tank flow, as in H-Coal and LC-Fining). The results obtained with this process are also given in Table 16.

INDIRECT LIQUEFACTION PROCESSES

In the indirect processes, coal and water are first converted to a mixture of CO and H_2 ("syngas"), partial combustion of the coal supplying the heat required and additional CO. This gas is at a higher

Table 15 Hydrogen use (on a percentage basis) in various coal liquefaction processes

	SRC I (Illinois No. 6)	SRC I (Kentucky No. 9)	SRC II (Kentucky No. 9)	EDS (Illinois No. 6)	(Ill Fuel oil
Hydrogen consumed, pounds per 100 pounds of coal	2.2	2.3	5.67	4.61	3.97
Hydrogen in C_4+ liquid, wt %	1.6	-6.9	12.2	27.1	12.6
Hydrogen in C_1-C_3 gas	70.4	70.4	62.2	40.1	48.1
Hydrogen used in heteroatom removal, wt %	28.2	36.5	25.6	32.8	39.3

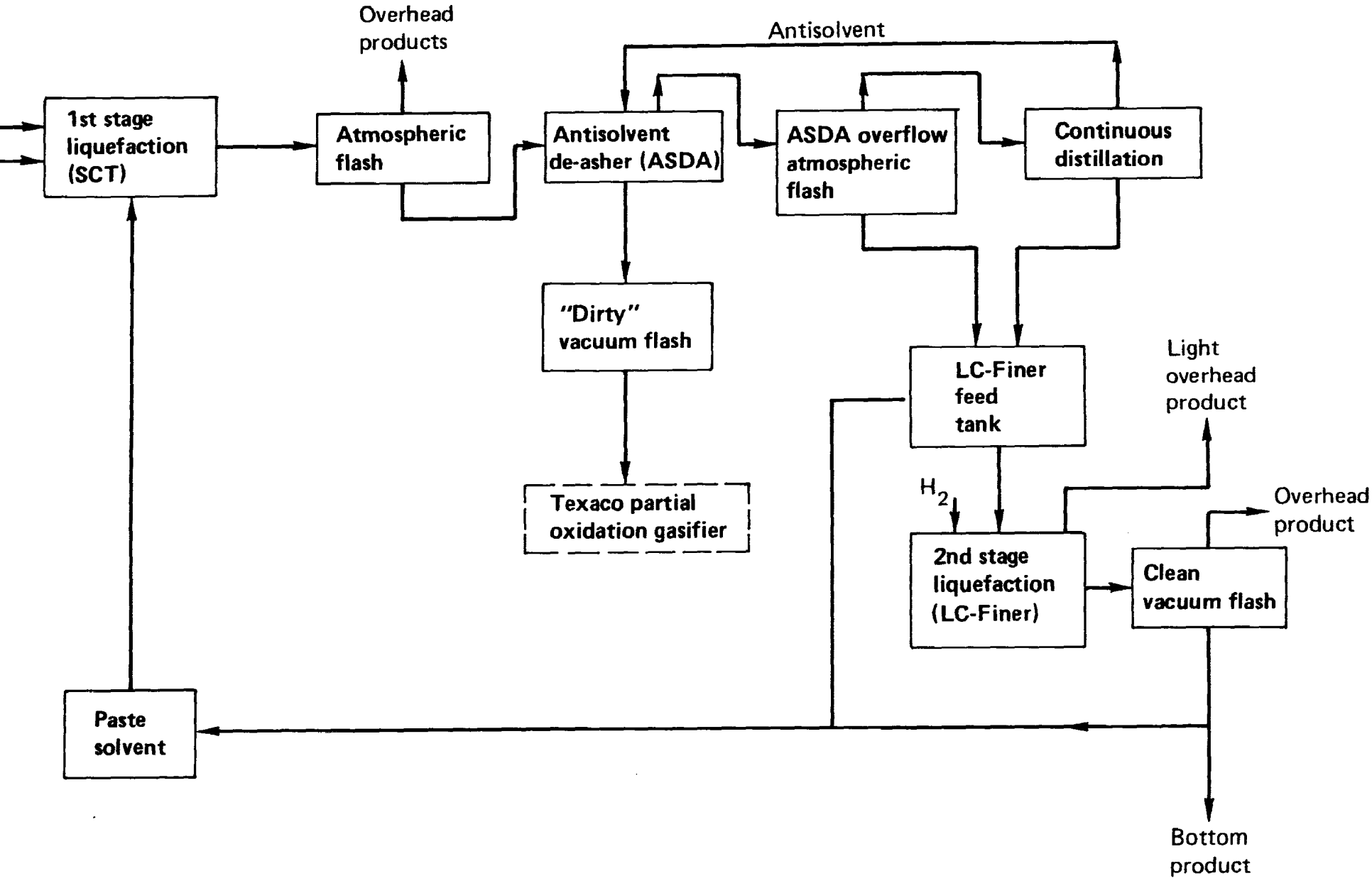


Figure 13 Lummus Two-Stage Coal Liquefaction process (Schindler, 1980)

Process	Hydrogen use, in pounds per 100 pounds of coal			
	Consumed	In CH_4+ liquid	In C_1-C_3 gas	For hetero-atom removal
Lummus Clean Fuels from Coal process (Illinois No. 6 coal)	3.4	1.24	1.09	1.07
Lummus Two-Stage Liquefaction process (Indiana V coal)	4.4	2.3	0.74	1.36

Source: Long et al. (1979); Schindler (1980).

heat. During production of the syngas, the heteroatoms that are not removed with the ash are converted into gases that can be removed from the syngas relatively easily, leaving it free of the sulfur and nitrogen that cause so much trouble in the refining of coal liquids by direct processes. Figure 14 is a flow diagram of a typical syngas plant with a Lurgi gasifier, in which only part of the new gas needs to be shifted to produce the H_2/CO ratio needed for each process.

The Fischer-Tropsch process used by SASOL in South Africa (Schreiner, 1978) converts the syngas into a complex mixture of hydrocarbons and oxygen-containing compounds that must be refined further to produce the end products required (fuels and chemicals). Table 17 shows the distribution of products from the SASOL plant.

The flow diagram of a typical Fischer-Tropsch plant is shown in Figure 15. In this plant, the reactor operates with a fluidized catalyst. The hydrocarbon products are mostly straight-chain olefins and paraffins, with almost no aromatics. Good diesel fuels are easier to produce from these products than from the highly aromatic products of direct liquefaction, but the use of the Fischer-Tropsch process for producing high octane gasoline presents problems due to the aliphatic nature of the product.

The production of gasoline from coal by the intermediate production of methanol is a simpler process. A flow diagram for such a plant is shown in Figure 16. The syngas is converted to methanol (CH_3OH) in a

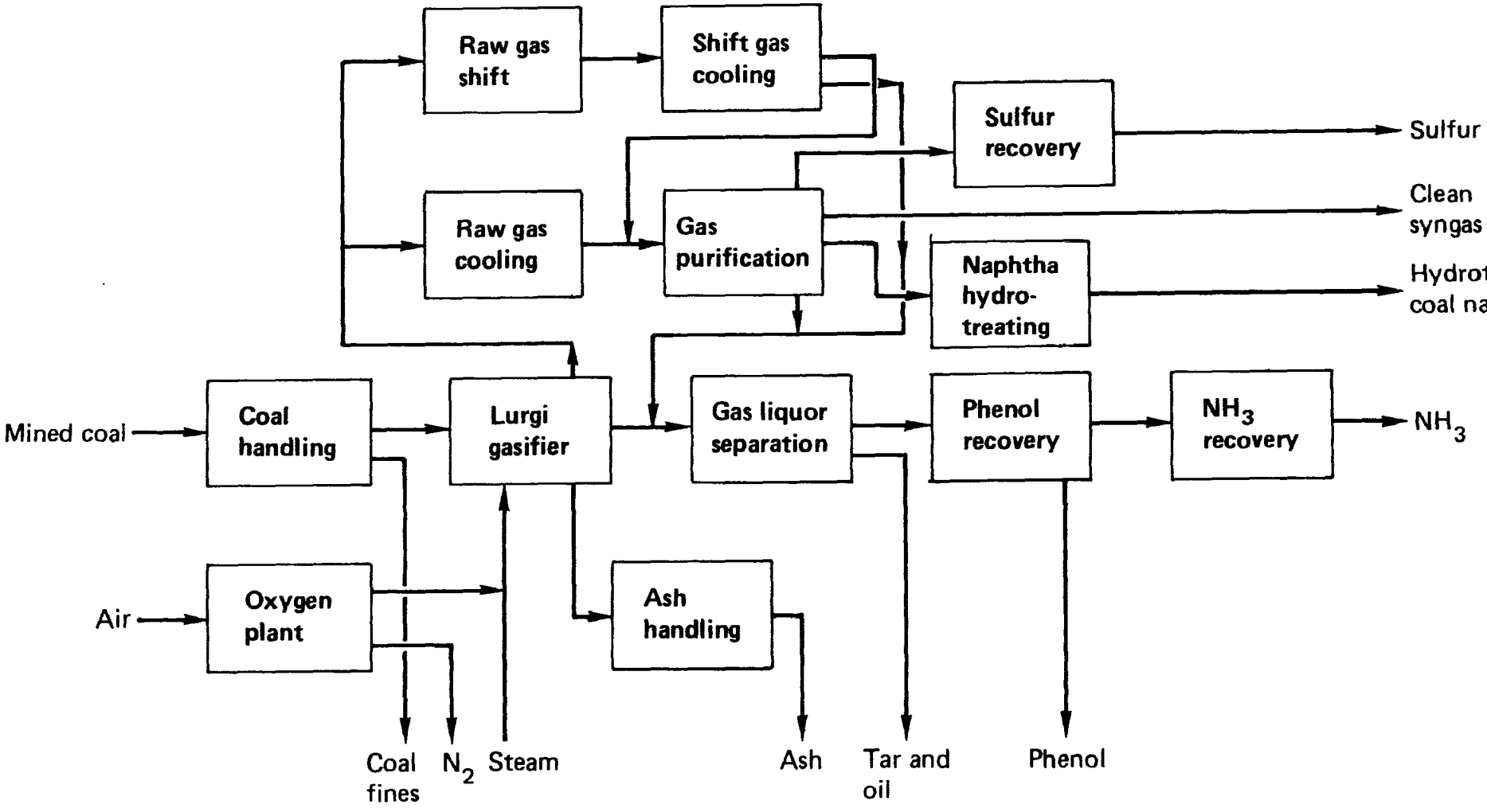


Figure 14 Typical coal gasification process, with Lurgi gasifier (Schreiner, 1978)

Component	Yield (Percent by weight)
Methane	10.7
Ethylene	3.7
Ethane	6.0
Propylene	11.6
Propane	2.0
Butylene	8.3
Butane	1.1
C_5-400°F	31.9
400-1000°F	13.4
1000°+F	0.6
Subtotal	89.3
Non-acid oxygenates	8.8
Organic acids	1.9
Total	100.0

Source: Hoogendoorn (1973).

line in a single step over a zeolite catalyst. To supply the hydrogen needed for hydrotreating the naphtha obtained from the gasifier, some of the gas is passed to a hydrogen recovery section. The first plant to produce gasoline by this process, to be built in New Zealand, is scheduled to go into production by the mid-1980s. In the methanol-to-gasoline step, the methanol is converted to water, gasoline, LPG,

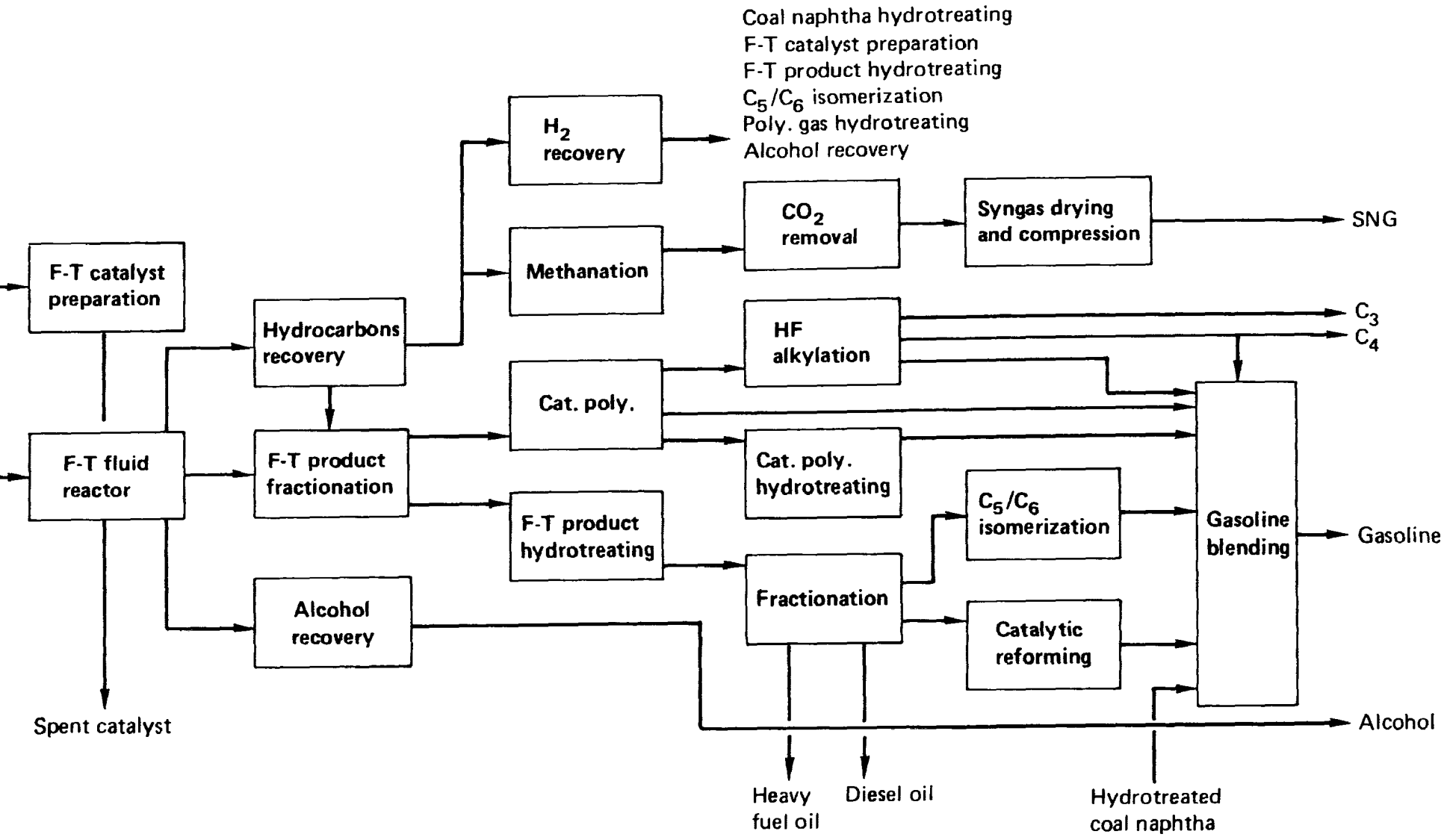


Figure 15 Typical Fischer-Tropsch process (Schreiner, 1978)

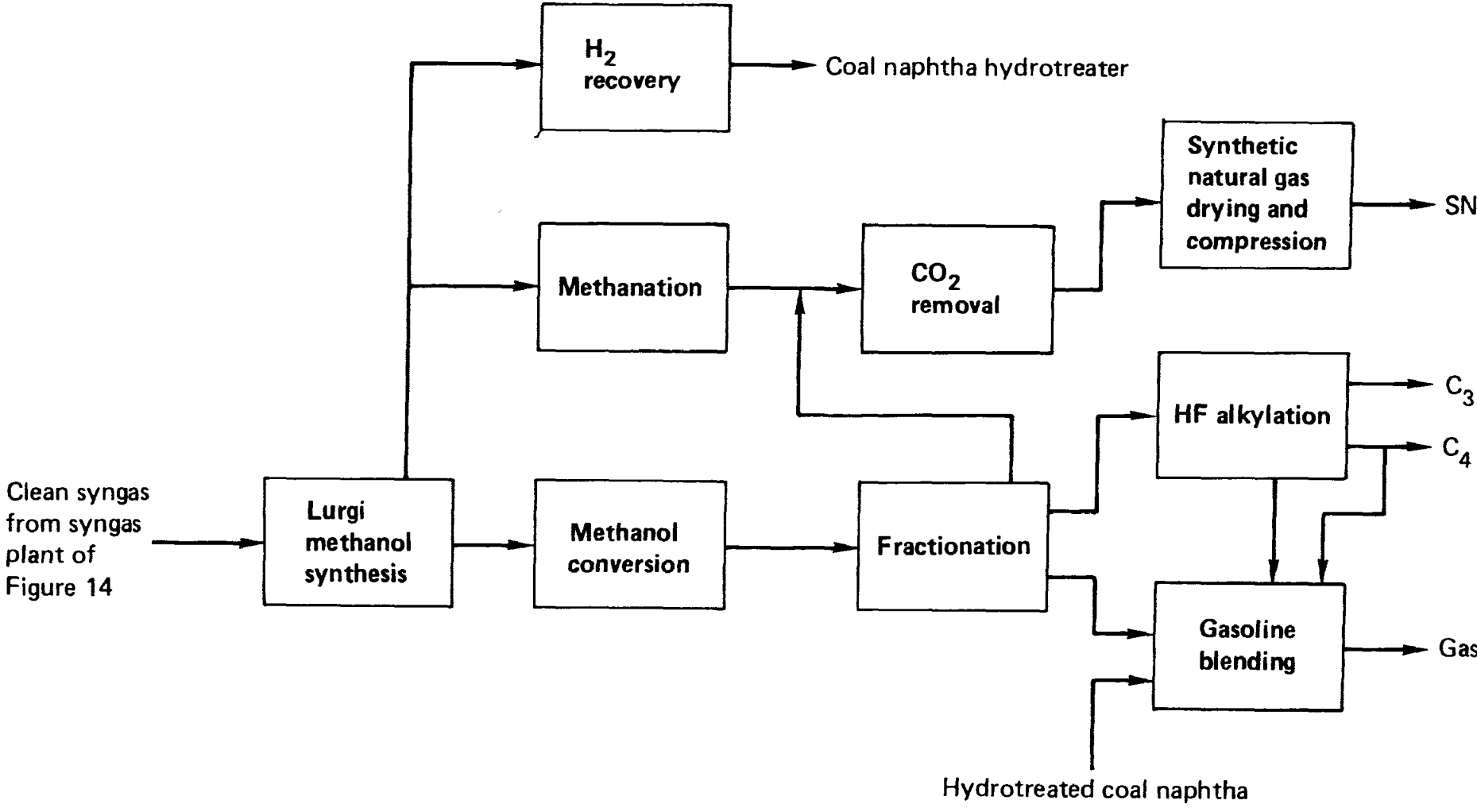


Figure 16 Flow design for methanol-to-gasoline plant (Schreiner, 1978)

Yield, wt % of methanol charged	
Hydrocarbons	43.6
Water	55.9
Hydrocarbon product composition, wt %	
C_1-C_2	1.4
C_3-C_4	18.7
C_5+ gasoline	79.9
Total	100.0
Finished product, wt %	
Gasoline, including alkylate	85.0
Liquefied petroleum gas	13.6
Fuel gas	1.4
Total	100.0
Physical properties of gasoline	
Research octane	
Clear	93
Leaded[a]	101
Reid vapor pressure, psig	9.0
Specific gravity	0.728
Sulfur, wt %	nil
Nitrogen, wt %	nil
Corrosion, copper strip	1A
Distillation temperatures, °F (ASTM)	
10%	114
30%	145
50%	198
90%	330
Composition, vol %	
Paraffins	53
Olefins	12
Naphthenes	7
Aromatics	28
Total	100
Motor octane	
Clear	83
Leaded[a]	90

BIBLIOGRAPHY

Eby, R. J. 1978. The Illinois Coal Gasification Group Project—COGAS Process. Proceedings of the 10th Synthetic Pipeline Gas Symposium, Oct. 30-Nov. 1, pp. 571-594. Sponsored by American Gas Association, U.S. Department of Energy, and International Gas Union. Chicago, Ill.: Gas Research Institute.

Epperly, W. R. 1978. EDS Coal Liquefaction Process Development, Phase 3-B/4. Annual Technical Progress Report. Washington, D.C.: U.S. Department of Energy (FE-2873-17).

_____. 1979. EDS Coal Liquefaction Process Development, Phase 4. Annual Technical Progress Report. Washington, D.C.: U.S. Department of Energy (FE-2893-35).

Fant, B. T. 1978. EDS--Coal Liquefaction Process Development, Phase 3A. Final Technical Report, Vol. 3. Washington, D.C.: U.S. Department of Energy (FE-2353-20).

Hoogendoorn, J. C. 1973. Experience with Fischer-Tropsch Synthesis at Sasol. Clean Fuels From Coal Symposium Papers, pp. 353-365. Chicago, Ill.: Institute of Gas Technology (CFFC-1).

Hydrocarbon Research, Inc. 1978. H-Coal Integrated Pilot Plant. Final Report, Vol. 1. Electric Power Research Institute. Palo Alto, Calif.: Research Report Center (EPRI-AF-681, Research Project 238-1).

Jackson, D. M., and B. K. Schmid. 1979. Production of Distillate Fuels by SRC-II. In Coal Conversion Technology, ed. A. H. Pelofsky. American Chemical Society Symposium Series, Vol. 110, pp. 55-68. Division of Industrial and Engineering Chemistry Winter Symposium. Washington, D.C.: American Chemical Society.

Johanson, E. S., and A. G. Comolli. 1978. Laboratory Program to Support H-Coal Pilot Plant Operations—PDU Run 5 Syncrude Mode Operation with Catalyst Addition and Withdrawal. Washington, D.C.: U.S. Department of Energy (FE-2547-19).

Jones, J. F. 1975. Char Oil Energy Development. Final Report, Vol. 1. FMC Corporation. Washington, D.C.: U.S. Department of Energy (FE-1212-T-9).

Kleinpeter, J. A., F. P. Burke, P. J. Dudt, and D. C. Jones. 1979. Process Development for Improved SRC Options: Interim Short Resi-

Project 1234-1-2).

_____. 1978. Annual Report. Solvent Refined Coal (SRC) Process: Operation of Solvent Refined Coal Pilot Plant at Wilsonville, Alabama. Stanford, Calif.: Electric Power Research Institute (EPRI-AF-867, Research Project 1234).

Lewis, H. E., W. H. Weber, G. B. Usnick, W. R. Hollenack, H. O. Blair, and R. G. Boykin. 1979. Solvent Refined Coal (SRC) Process: Operation of SRC Pilot Plant at Wilsonville, Alabama. Stanford, Calif.: Electric Power Research Institute (EPRI-AF-1287, Research Project 1234-1-2).

Long, R. H., M. Peluso, and A. A. Simone. 1979. The C-E Lummus Clean Fuel From Coal Process. Paper presented at Coal Technology '79 Conference, Houston, Tex., Nov. 8. (Available from C-E Lummus Co., Marketing Services Dept., 1515 Broad Street, Bloomfield, N.J. 07003.)

Longanbach, J. R., J. R. Droege, and S. P. Chauhan. 1978. Short Residence Time Coal Liquefaction. Stanford, Calif.: Electric Power Research Institute (EPRI-AF-780, Research Project 779-5).

National Research Council. 1977. Assessment of Technology for the Liquefaction of Coal. Ad Hoc Panel on Liquefaction of Coal, Committee on Processing and Utilization of Fossil Fuels, Commission on Sociotechnical Systems. Washington, D.C.: National Academy of Sciences.

Oberg, C. L., and A. Y. Falk. 1979. Coal Liquefaction by Flash Hydropyrolysis. Paper No. 81b, presented at 72nd Annual Meeting of American Institute of Chemical Engineers, San Francisco, Calif., Nov. 28. (Available from Engineering Societies Library, 345 E. 47th Street, New York, N.Y. 10017.)

Schall, J. 1979. Compilation and Assessment of SRC Experience: Data Book. Stanford, Calif.: Electric Power Research Institute (EPRI-AF-1019, Research Project 987-1).

Schindler, H. D. 1980. Advanced Two-Stage Liquefaction Process. Paper presented at U.S. Department of Energy meeting, Albuquerque, N.M., February 26.

Schreiner, M. 1978. Research Guidance Studies to Assess Gasoline from Coal by Methanol-to-Gasoline and Sasol-Type Fischer-Tropsch Technologies. Washington, D.C.: U.S. Department of Energy (EF-2447-13).

Stein, T. R., J. G. Bendoraitis, A. V. Cabal, R. B. Callen, M. J. Dabkowski, R. H. Heck, H. R. Ireland, and C. A. Simpson. 1977. Upgrading of Coal Liquids for Use as Power Generation Fuels. Electric Power Research Institute. Palo Alto, Calif.: Research Report Center (EPRI-AF-444, Research Project 361-2).

Stein, T. R., A. V. Cabal, R. B. Callen, M. J. Dabkowski, R. H. Heck, C. A. Simpson, and S. S. Shih. 1978. Upgrading of Coal Liquids for Use as Power Generation Fuels. Electric Power Research Institute. Palo Alto, Calif.: Research Report Center (EPRI-AF-873).

Sullivan, R. F., B. E. Stangeland, and H. A. Frumkin. 1979. Refining of SRC-I and SRC-II. Paper presented at Refining of Syncrudes Contractors Conference, Richmond, Calif., May 7-8, sponsored by U.S. Department of Energy.

Synthetic Fuels. 1979. Economics for SRC-I and SRC-II Demonstration Plants Compared. Synthetic Fuels 16(2)(June):4-34 to 4-39. Denver, Colo.: Cameron Engineers.

Whitehurst, D. D. 1978. A Primer on Chemistry and Constitution of Coal. American Chemical Society Symposium 71: Organic Chemistry of Coal, pp. 1-35. Washington, D.C.: American Chemical Society.

Whitehurst, D. D., M. Farcasiu, and T. O. Mitchell. 1976. The Nature and Origin of Asphaltenes in Processed Coal. Electric Power Research Institute. Palo Alto, Calif.: Research Report Center (EPRI AF-252).

Whitehurst, D. D., M. Farcasiu, T. O. Mitchell, and J. J. Dickert, Jr. 1977. The Nature and Origin of Asphaltenes in Processed Coal. Electric Power Research Institute. Palo Alto, Calif.: Research Report Center (EPRI-AF-480, Research Project 410-1).

5 OIL SHALE EXTRACTION PROCESSES AND PRODUCTS

Oil shale is a layered gray-brown sedimentary rock known as marlstone, formed millions of years ago in freshwater lakes. The oil in the shale is in kerogen, a complex material composed mainly of carbon, hydrogen, oxygen, sulfur, and nitrogen. The large kerogen molecules are bound to each other by oxygen, sulfur, and hydrocarbon bridges in a three-dimensional network that extends through the mineral portions of the shale, binding them together. The amount of kerogen in a given deposit depends on how much organic material was present in the lake beds.

The oil content of shale denotes its quality. Shale with an oil content of 10 gallons per ton (about 4 percent by weight) is considered low-grade shale. Shale with an oil content of 26 gallons per ton (about 10 percent) is considered medium grade, and shale with an oil content of 36 gallons per ton (about 14 percent) is considered high grade.

In considering the ultimate use of shale oil, it is necessary to understand the retorting processes for decomposing and separating the kerogen from the rock. The shale can be retorted either in situ underground, or after it is mined and brought to the surface.

It is highly desirable that both types of retorting be developed, since their combined use will lead to optimal resource recovery. A preference of one over the other is not indicated or intended in this report. Neither has yet been demonstrated on a full commercial scale, although the probability of success for both is high.

This chapter deals with the retorting processes that have been brought to the point at which they are being considered for eventual commercialization. The first section of the chapter covers surface retorting, the second section covers in situ retorting, and the third section deals with the physical and chemical properties of the raw liquids produced by these processes.

The Lurgi-Ruhrgas (LR) process distills hydrocarbons from oil shale by bringing raw shale in contact with hot fine-grained solid heat carriers. The best heat carrier is the spent shale, but rich shales, which deteriorate into a fine powder, must be supplemented by more durable materials such as sand.

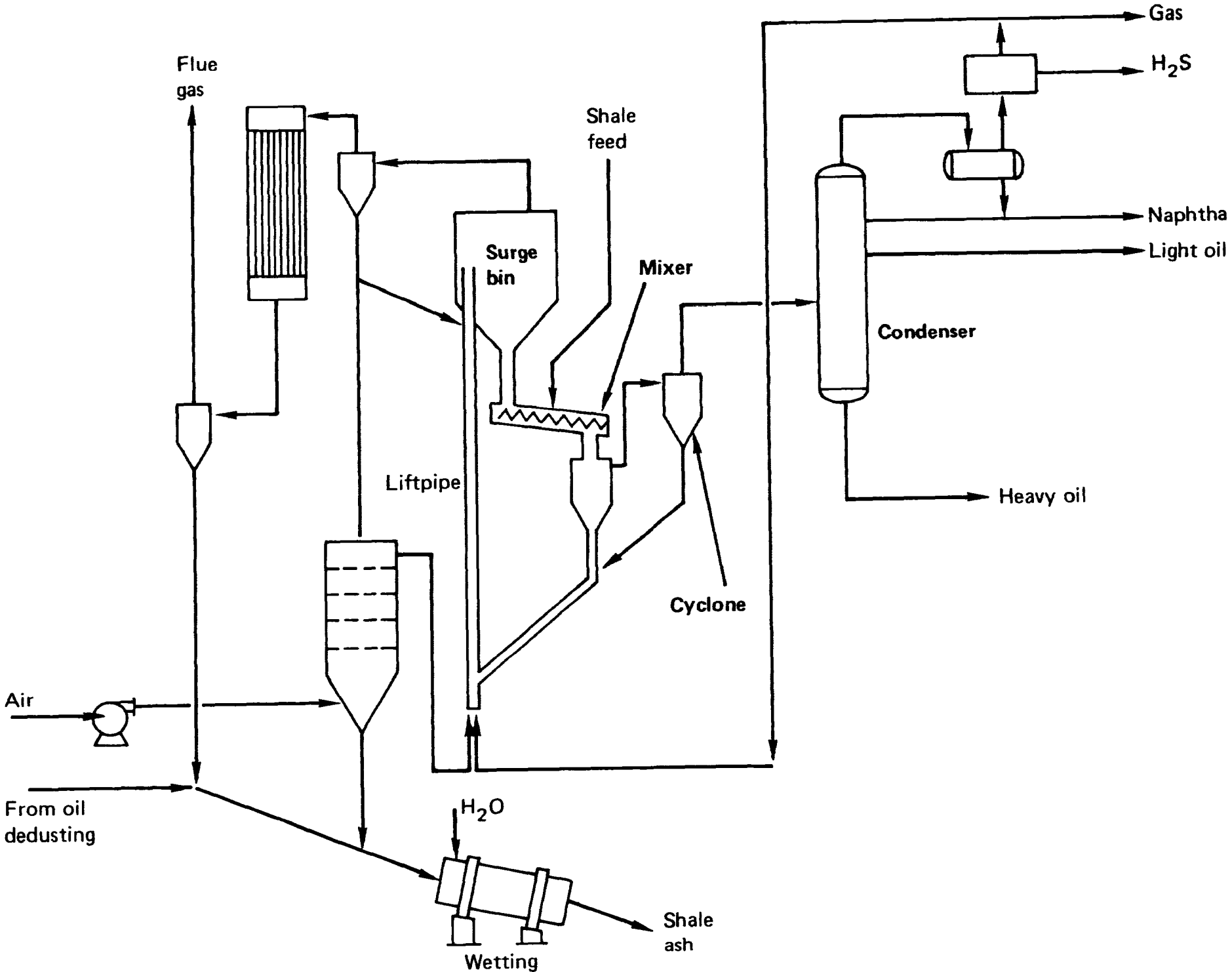
In the LR process (Figure 17), the pulverized oil shale and heat carrier are brought into contact in a mechanical mixer such as a screw conveyor. In pilot plant tests, the shale was first crushed to a maximum size of one-fourth to one-third of an inch, but larger commercial units might process particles as large as half an inch (Rammler, 1970). The gas and oil vapors are then cleaned of dust in a hot cyclone; the dust is recycled and the oil is separated by condensation. Retorted shale from the mixer passes through a hopper to the bottom of a lift pipe, with the dust from the cyclone. Preheated air introduced at the bottom of the pipe carries the solids up to the surge bin, during which time they are heated by the combustion of the residual carbon in the shale to about 1,000°F. (If the residual carbon is insufficient for this, fuel gas is added.) In the surge bin, the hot solids separate from the combustion gases and return to the mixer, where they are brought in contact with new oil shale, completing the cycle.

Pilot plant tests have produced high yields. Oil recovery greater than 100 percent Fischer assay has been achieved from Colorado shale with an oil content of about 30 gallons per ton. (The Fischer assay procedure is a rigidly defined test, the results of which serve as a baseline for comparing different extraction processes.) Since no combustion occurs in the mixer retort in this process, the product gas from the mixer has a high calorific value.

As the LR process can handle very small particle sizes, it can be modified for a variety of shale feedstocks. The system is also mechanically simple; only the mixer is of concern because it must operate reliably in a harsh environment. Two serious problems result from the movement of dust through the system, however. One is the accumulation of combustible dust in the transfer lines, increasing the likelihood of fires and plugging. The other is entrainment of dust in the oil produced; most of the dust is removed in the hot cyclone, but some is inevitably carried over in the retort product.

There are ways of dealing with the latter problem. When the crude oil from the LR process is fractionated, the dust concentrates in the heaviest fraction, and can be dealt with by diluting and filtering this fraction or by recycling it to the mixer.

The LR process, developed in the 1950s for the low-temperature flash-carbonization of coal, has been tested on European and Colorado oil shale


Flue gas
Shale feed
Surge bin
Mixer
Liftpipe
Cyclone
Gas
H_2S
Naphtha
Light oil
Condenser
Heavy oil
Air
From oil dedusting
H_2O
Shale ash
Wetting

near Essen, Germany. Two 850-ton-per-day plants for carbonizing brown coal were installed in Yugoslavia in 1963, and a large plant that uses the LR process to produce olefins by cracking light oils has been built in Japan (Rammler, 1969, 1970).

Superior's Multi-Mineral Process

The multi-mineral process is a four-step operation that produces four coproducts: nahcolite, (sodium bicarbonate, $NaHCO_3$), shale oil, alumina, and soda ash (Figure 18). The process was developed by Superior Oil for shale that contains recoverable concentrations of oil, nahcolite, and dawsonite (a sodium-aluminum salt, $Na_3Al(CO_3)_3.Al(OH)_3$). Superior has operated a pilot plant of this type in Cleveland, Ohio.

The underground shale in Superior's property is mined in panels by the room and pillar method and delivered to the surface by conveyor. After processing, the spent shale is returned to the mined-out panels to stabilize the pillars.

The nahcolite is in the form of discrete nodules that are more brittle than the shale. It is recovered by secondary crushing and screening, followed by a specialized process called "photosorting" that recovers nahcolite product of greater than 80 percent purity. After the nahcolite is removed, the shale is pyrolyzed using the McDowell-Wellman process. The unique continuous-feed, circular-moving-grate retort used in this process is a proven, reliable piece of hardware that provides accurate temperature control, separate process zones, and a water seal that eliminates environmental contamination.

The dawsonite in the shale is decomposed in the retort to aluminum oxide and soda ash. After the shale has been leached with recycled liquor and makeup water from the saline subsurface aquifer, the liquid is seeded and the pH lowered to recover the alumina. The soda ash is recovered by evaporation. The leached spent shale is then returned to the mine and the liquor is returned to the process.

Paraho Process

The Paraho retort is a stationary, vertical, cylindrical kiln of mild steel, refractory-lined, in which the shale is brought to temperature by a counterflow of combustion gases (Figure 19). As the shale (fed in at the top along a rotating "pantsleg" distributor) moves down through the retort, the rising stream of hot gas breaks down the kerogen to oil, gas, and residual carbon. The oil and gas are drawn off, and the resid-

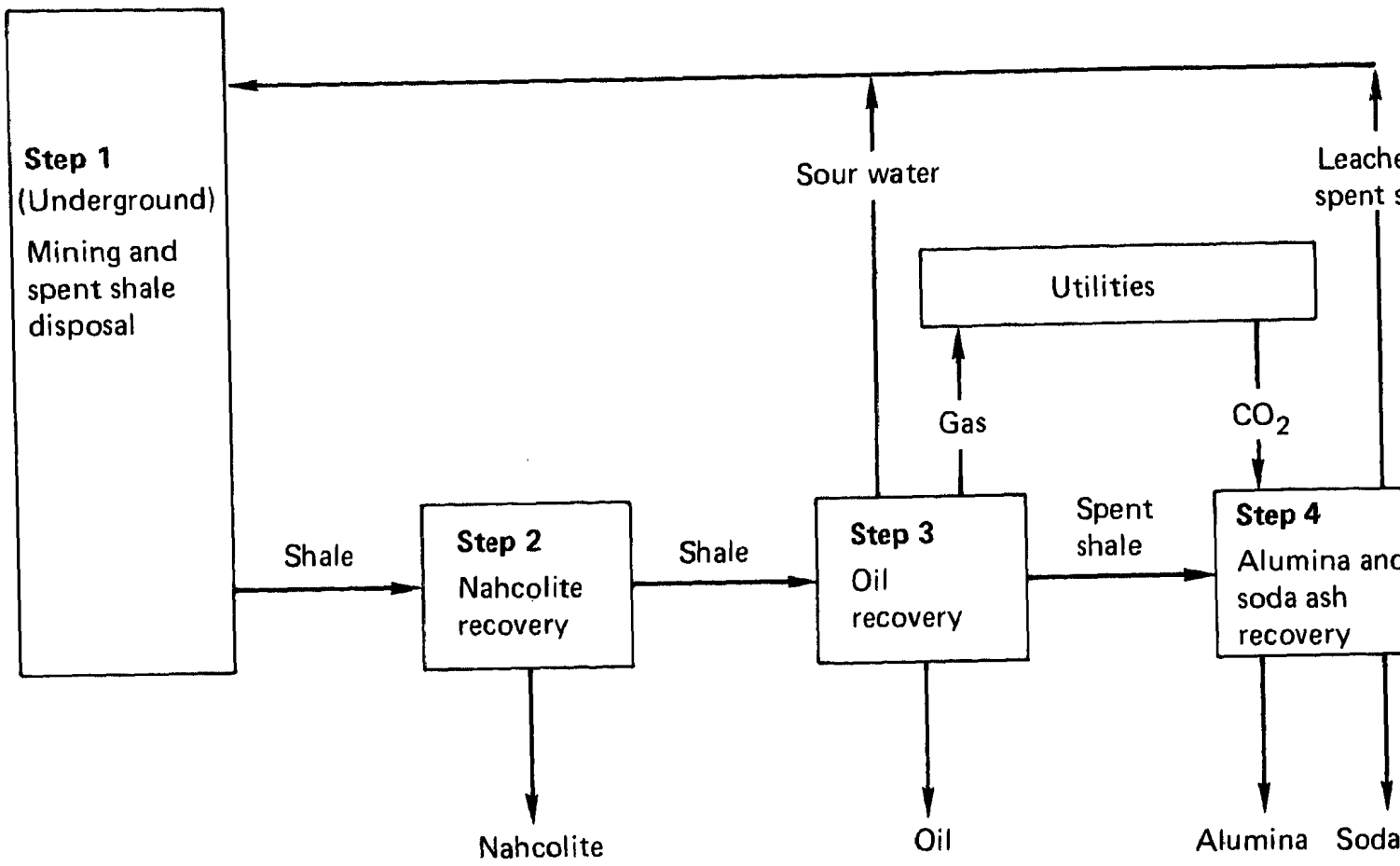


Figure 18 Superior Oil multi-mineral process (Superior Oil, 1977)

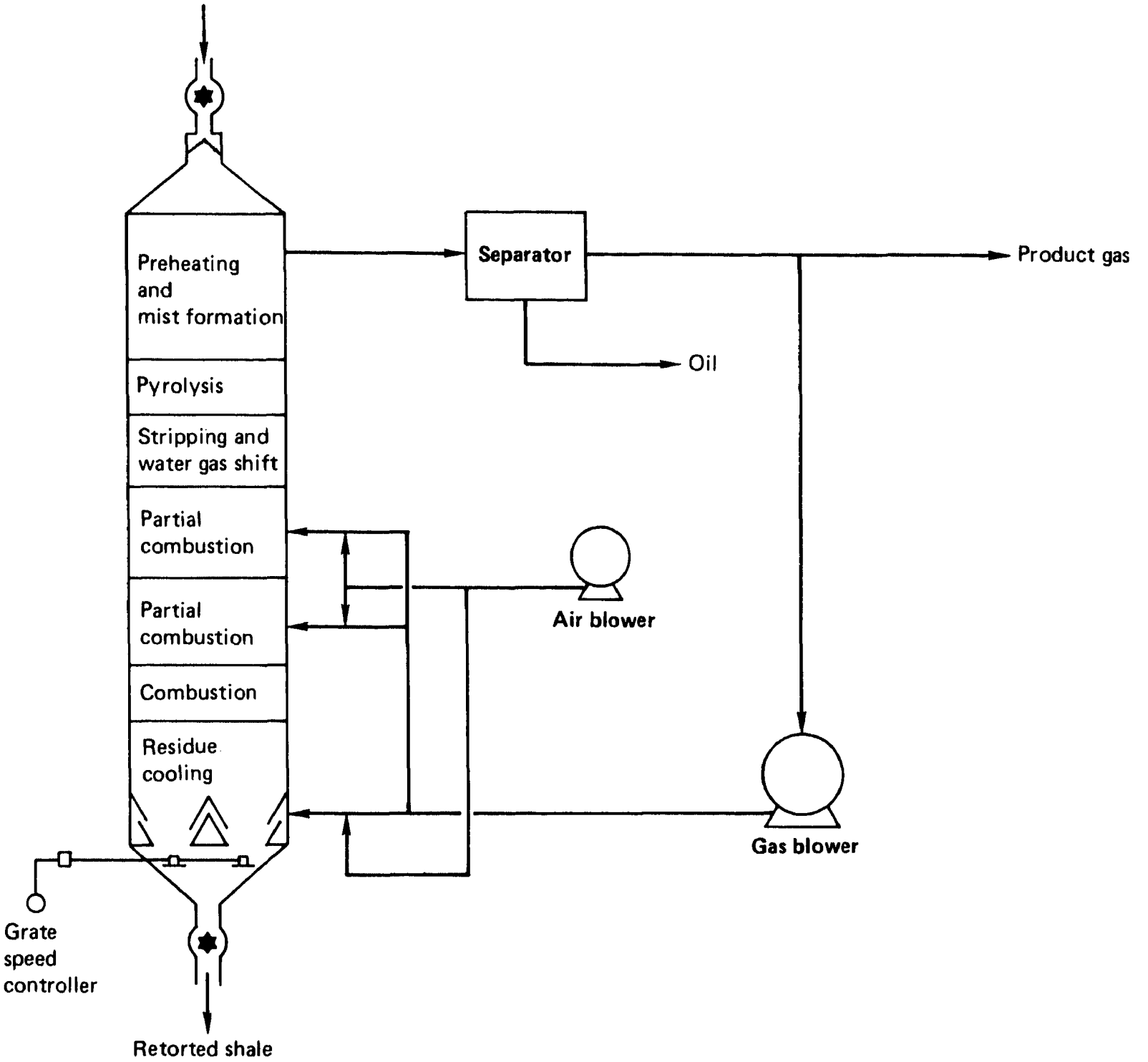


Figure 19 Paraho process for extracting shale oil (Cameron Engineers, 1975)

The Paraho process, developed by Development Engineering Incorpor ated (DEI), is conceptually similar to the internal-combustion retorti process used by the Bureau of Mines, but there are significant differ- ences in the shale-feed mechanism, the combustion gas distributors, and the spent shale discharge grate. It is possible with this process to use either direct or indirect heating. Most of the development wor so far has been carried out with the direct heating system described here.

Research and development on the Paraho retort, begun by Paraho De opment Corporation (DEI's parent company) in August 1973, continued un April 1976 under the sponsorship of 17 energy and engineering companie In 1978, Paraho delivered 100,000 barrels of raw shale oil to the U.S. Navy for defense testing purposes.

The Paraho kiln has most of the advantages common to internal- combustion retorts. It can handle shale with a feed size of at least 3 inches, keeping crushing and screening costs at a minimum. A high t mal efficiency results from burning the residual carbon and recovering sensible heat from the spent shale. The process is mechanically simpl requiring little auxiliary equipment. No water is required for produc cooling. To date, more than 100 days of continuous operation have bee achieved, with oil recoveries of better than 90 percent of Fischer ass

Tosco II Process

The Tosco II process[a] uses ceramic balls to heat the oil shale. The shale, crushed to less than half an inch in size, is introduced throug multiple lift pipes in which streams of hot gas elevate and preheat it about 500°F (Figure 20). The shale is then fed to a rotating drum wit half-inch ceramic balls that have been heated to about 1200°F. Inside the rotating drum, which is about 8 feet in diameter and 15 feet long, the balls turn the kerogen in the shale to oil vapor and gas and crush the shale to a fine black powder. The balls and crushed shale, now at about 950°F, are fed to a perforated rotating drum (trommel) in which the shale and the ceramic balls are separated. The spent shale drops through the holes in the drum, is cooled, and is then disposed of. Th balls return to the ball heater, where they are reheated with gas from the shale, completing the cycle.

---

[a]This process is a refinement of the Aspeco Process developed by the Swedish inventor Olaf Aspegren. Although Aspegren patented the concep he did not reduce it to practice (Aspegren, 1952). The Oil Shale Cor- poration (Tosco) purchased the patent rights in 1952.

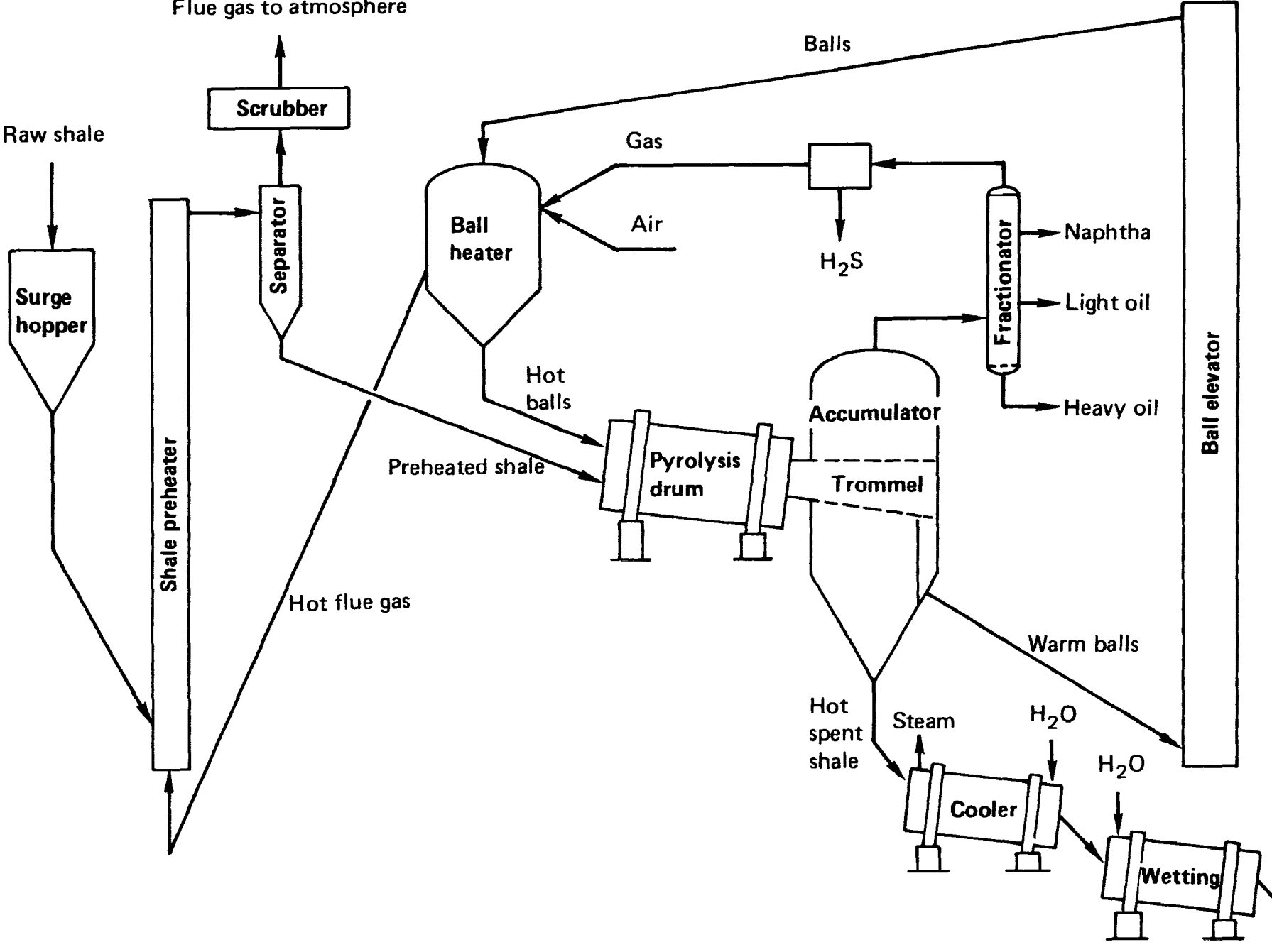


Figure 20 Tosco II process for extracting shale oil (Cameron Engineers, 1975; Sladek,

and heavier hydrocarbons is about 100 percent of Fischer assay (Hendrickson, 1974). The retort gas has a heating value similar to that of Fischer assay gas, since there is no combustion in the pyrolysis drum; most of the gas is used in the ball heater.

Field operations using a retort with a shale feed rate of about 1 tons per day were carried out in Colorado during 1967-69 and 1971-72.

Union Oil Retorting Processes

Union Oil, active in retort research and development since the late 1940s, has three designs: the "A" retort, in which the internal combustion of the gas and residual carbon from the shale provide the heat for the process (direct heating); the "B" design, in which the shale is heated indirectly by a recycled stream of externally heated gas (Figure 21); and the Steam-Gas Recirculation (SGR) retort, in which the heat carrier for the process is generated in a separate vessel by gasifying the residual carbon with air and steam.

Union's retorts have been characterized as "continuous, underfeed countercurrent retorts" (Hartley, 1958). In all three, the shale is introduced at the base, travels upward through the retort, and is discharged at the top. The gaseous heat carrier (air, recycle gas, or syngas) enters at the top and exits from the bottom. The product oil flows down through the moving bed of shale to a pool at the bottom of the retort and is withdrawn from the top of that pool. Serving as a seal, the pool prevents air from leaking into the retort and also acts as a settling basin for the entrained fines.

A unique design feature of the Union retorts is the "rock pump" that pushes shale up through the retort. In an early patent (Berg, 1947), the rock pump was mechanical, providing motion to the shale bed through a series of gears and cams. The modern hydraulic rock pumps have large cylinders that take the crushed shale from the feed chutes and pump it into the retort.

In the "A" process, the thermal efficiency is high because sensible heat is recovered from the oil, gas, and spent shale. The oil recovery is about 84 percent of Fischer assay, but the product gas is a low-energy fuel (with a heating value of about 100 Btu per standard cubic foot) due to its dilution by combustion products. In the early tests, the high temperatures caused the agglomeration of the spent shale ash, requiring the use of hollow sodium-cooled "plows" to break up the clinkers. Better temperature control in later designs has made the plows unnecessary.

In the "B" process, the product gas exiting from the bottom of the

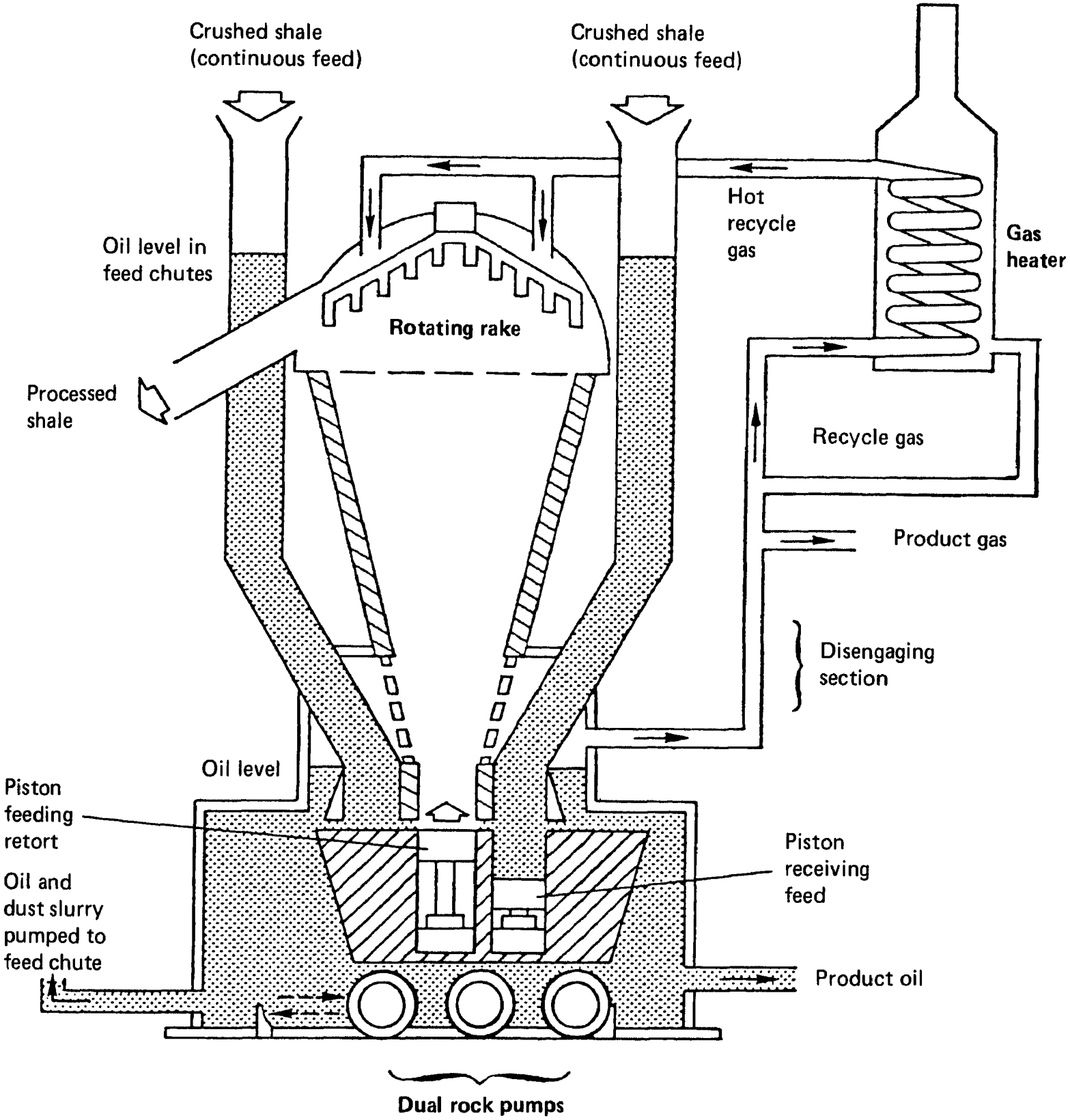


Figure 21 Union B process, showing indirect heating of shale (Duir, 1977; Hopkins, 1976)

the retort. The recycle stream and the product stream are not diluted by combustion products, as they are in the "A" process. The absence of combustion inside the retort offers other advantages. Temperature control is better and, as a result, there is no clinkering problem. In addition, the oil yields are higher than in the "A" process, reaching 100 percent of Fischer assay (Hartley, 1974).

Union's latest retort, the SGR, is basically a "B" retort with auxiliary equipment for recovering energy from the residual carbon by gasification.

Union's experience with the three processes has been as follows:

- The early development work on the "A" retort included the operation of a 2-ton-per-day prototype and a 50-ton-per-day pilot plant at Wilmington, California. Additional operating experience has been obtained from a semiworks unit near Grand Valley, Colorado, with a design capacity of about 350 tons per day. Production rates higher than this were achieved soon after startup in March 1957. By the time the field tests on the latter unit were completed in August 1958 the capacity had been increased, allowing continuous operation at rates of up to 1200 tons per day (Hartley and Hemmen, 1957; Hartley, 1958).

- Since 1971, a nominal 6-ton-per-day pilot retort has been operated in the "B" mode and the SGR mode at the Union Research Center in Brea, California.

IN SITU RETORTING PROCESSES

During the past 10 years, an increasing amount of research has been directed toward the production of oil from shale in situ, or underground.

Most oil shales have very little if any natural permeability,[a] and this makes it nearly impossible to recover oil from them in situ. Two techniques have been proposed for producing some permeability in such formations. With the modified in situ technique, part of the shale bed is removed to create a void that will allow fracturing the rest of the bed with explosives. With the true in situ technique, no mining or other void-producing preparation is required; the permeability is produced with well bores from the surface.

Occidental Petroleum Process

Occidental Petroleum Corporation is developing a vertical modified in

shale in the chimney is removed, air is blown down through the remaining crushed shale and the top is ignited with a burner that can be fueled with shale oil or off-gas from other retorts. On ignition, the burner is withdrawn and steam is mixed with the inlet air to control the process. The liquid and gaseous products flow to the bottom of the chimney, leaving the carbon in the shale behind as the main source of fuel for the slowly advancing flame front.

Occidental Petroleum began a series of field tests on its modified in situ process at Logan's Wash in Debeque, Colorado, in 1972. Three retorts, 30 feet across and 72 feet deep, each containing 6,000 to 10,000 tons of oil shale, were created. The subsequent series of tests are being used as the basis for three commercial-scale retorts that are 30 to 40 times larger. Occidental Petroleum has also leased Colorado federal oil shale tract C-b for shale oil recovery with modified in situ technology on a commercial scale. Full-scale production of 57,000 barrels per day was originally planned for 1983, but plans now call for full-scale production in 1987.

LETC Process

The Department of Energy at its Laramie Energy Technology Center (LETC) is sponsoring several field projects to demonstrate the technical and economic feasibility of shale oil recovery by in situ methods. The projects include in-house research and joint government-industry efforts (Table 19).

LETC began its study of true in situ processes in the early 1960s with laboratory tests, simulated pilot-plant tests on 10-ton and 150-ton retorts, and field tests at Rock Springs, Wyoming. The results of the tests were encouraging, demonstrating that it was possible to move a self-sustaining combustion zone through an oil shale formation and produce oil. The technique appears, at this stage, to be more suitable than the other processes described so far for thin oil shale formations.

The underground shale is prepared for the LETC process by first boring injection and production wells into the shale (Figure 23) and then increasing the permeability of the formation by conventional fracturing techniques. (LETC tried electrolinking, well-bore shooting, and hydraulic fracturing, and found that the sequential use of hydraulic fracturing and explosives succeeded best.) Once the formation has been fractured, hot gases are forced into it to heat the area around the injection point. As the desired temperature is reached and air is substituted for the hot gas, combustion begins and becomes self-sustaining across a front that gradually moves through the bed. As retorting progresses, oil and gas products are pumped out through the production well.

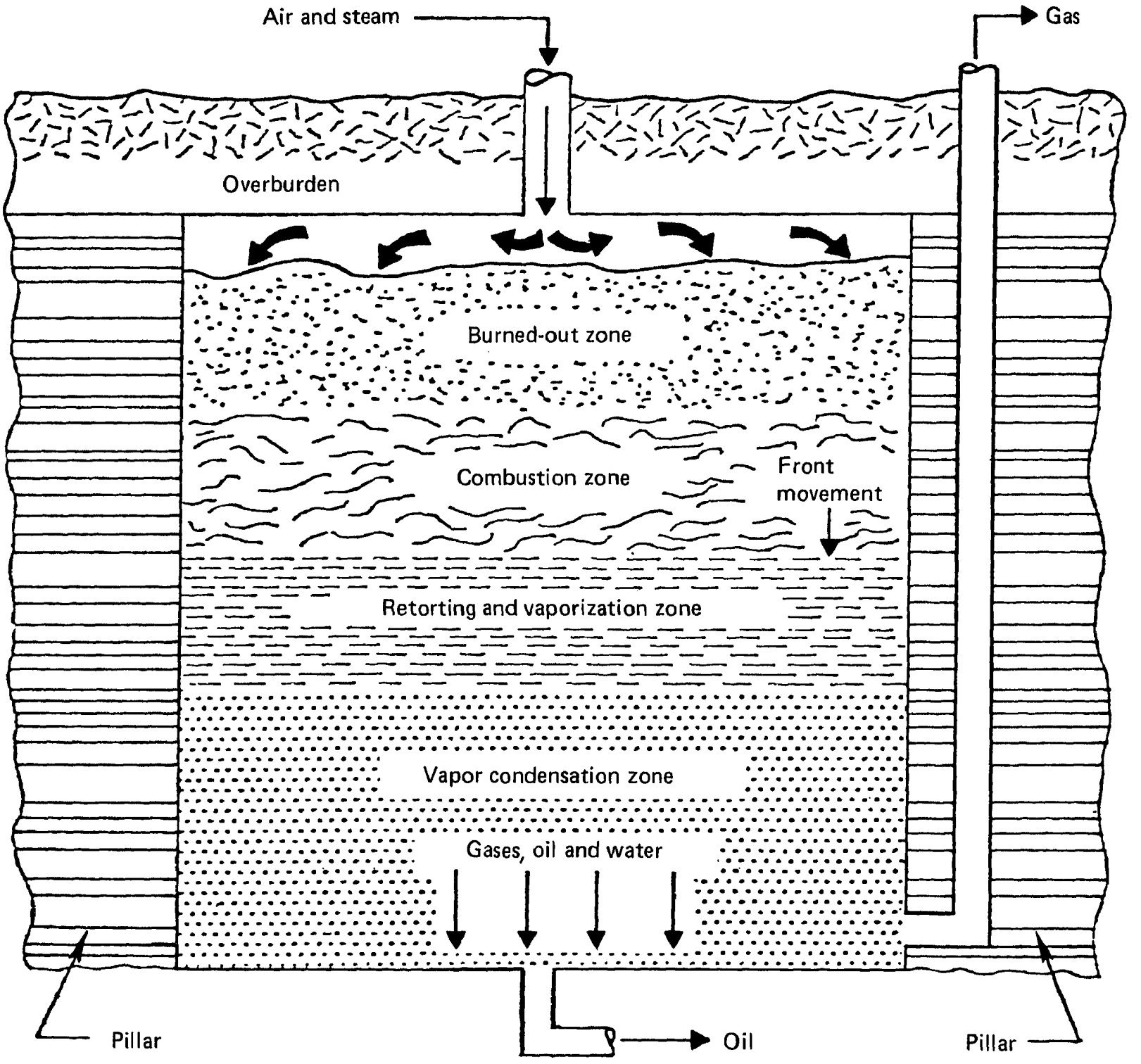


Figure 22 Modified in situ retort of Occidental Petroleum (McCarthy and Cha, 1976; Sass and Lumpkin, 1977)

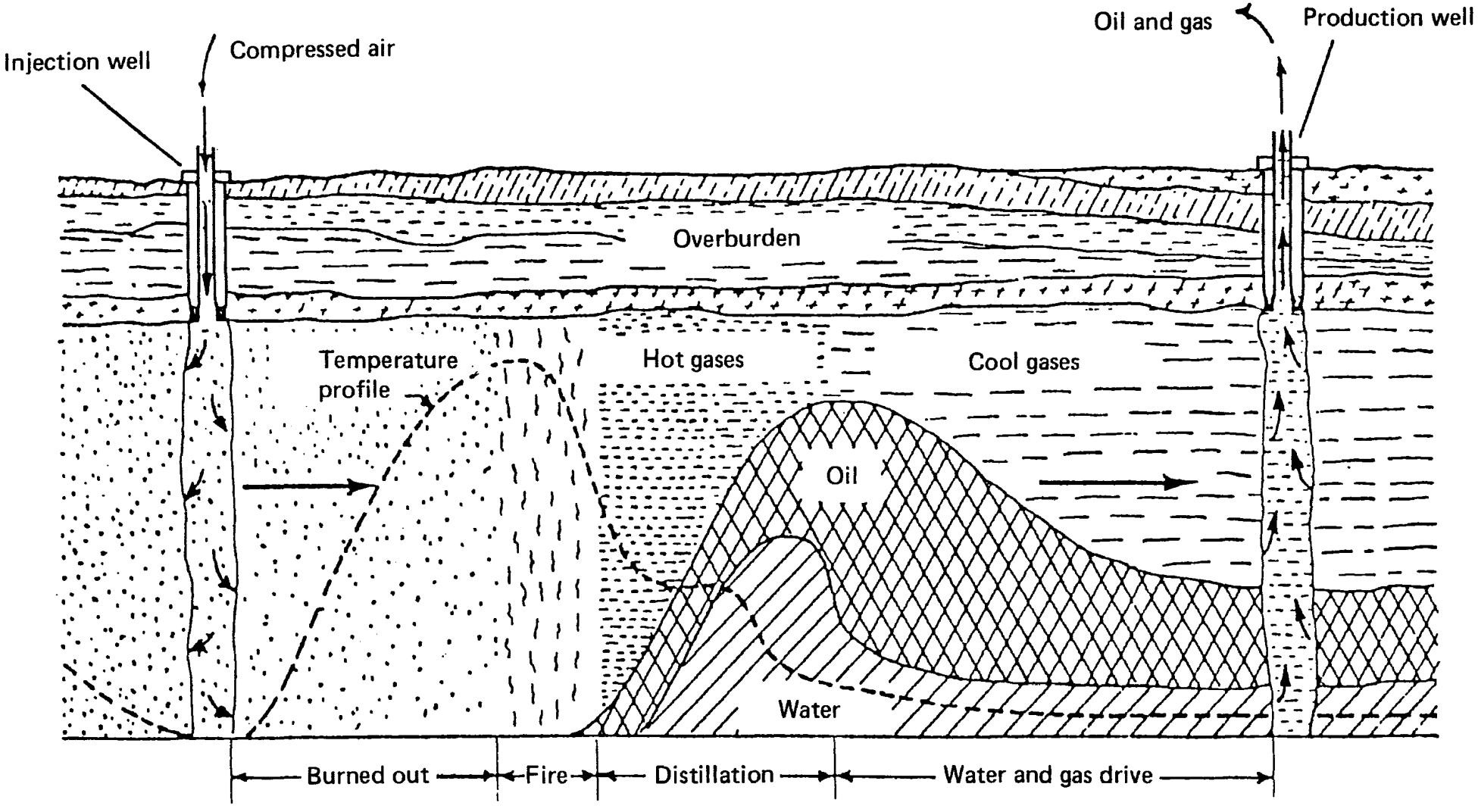


Figure 23 Laramie Energy Technical Center (LETC) in situ retorting process (Sladek, 1975)

	Dow Chemical Company	Talley Energy Systems, Inc.
Resource site		
Location	75 miles NE of Detroit, Mich.	11 miles west of Rock Springs, Wyo.
Anticipated size, in acres	1	163
Status	Owned	Leased from Rocky Mountain Energy
Geological formation	Antrim oil shale	Green River Oil Shale
Member	Not applicable	Tipton
Zone	Not applicable	Upper
Age, years	260 million	50 million
Structural basin	Michigan	Green River
Target zone thickness, feet	200	40
Overburden above zone, feet	1200	360
Average oil content, gallons per ton	10	23
Average sulfur content, percent	3.5	0.7
Process Technology		
Category	True in situ	True in situ
Method	Explosive fracturing; additional hydraulic fracturing; no mining	Explosive fracturing; additional hydraulic fracturing; no mining
Special problems	Project depth; low hydrogen organics; sulfur content	Creating permeability in fissile shale
Special potentials	Shale gasification; very extensive resource	Shallow thin-seam recovery

Source: Dockter (1978).

		Company
53 miles north of Grand Junction, Colo.	61 miles NW of Grand Junction, Colo.	31 miles NE of Grand Junction, Colo.
4	640	3
Owned	Leased from Utah	Owned
Green River Oil Shale Parachute Creek Leached 50 million Piceance Creek	Green River Oil Shale Parachute Creek Mahogany 48 million Uinta	Green River Oil Shale Parachute Creek Mahogany 48 million Piceance Creek
550 800	30 0-100	300 400
28	25	16
0.7	0.7	0.7
Solution injection	Modified horizontal	Modified vertical
No explosives; no mining	Explosive fracturing; no mining	Explosive fracturing; limited mining
Saline aquifer; waste water disposal	Surface disturbance	Mined shale disposal
Utilizing natural porosity	Shallow thin-seam recovery	Deep thick-seam recovery

modified in situ process that has not yet been field-tested.

The process, shown in Figure 24, is conceived as essentially continuous; as one part of a formation (approximately 100 feet across and 1000 feet deep) is being retorted, adjacent sections are in various stages of preparation. To prepare a section for retorting, it would be blasted to loosen and break up the shale, and part of the rubble would be removed to the surface.

No field testing has yet been done, but large-scale tests to simulate below-ground processing, along with a variety of small-scale tests and mathematical modeling programs, have been carried out.

According to the Livermore Laboratory, the process could be used on much leaner deposits than those now being considered for above-ground retorting (e.g., deposits with an oil content of 20 gallons per ton, but rather deep shale formations would be required.

PHYSICAL AND CHEMICAL DATA ON RAW SHALE OIL FROM VARIOUS RETORTING PROCESSES

Table 20 lists the available physical and chemical properties of whole raw shale oil from different retorting processes, and Tables 21-23 present some fractional analyses that are helpful in understanding the concentrations of the types of compounds in these shale oils as a function of boiling range.

On examining the physical properties of raw shale oils, it can be seen that the principal variations are those in boiling range, pour point, and viscosity. In general, shale oils have a somewhat narrower boiling range than most petroleum crudes because they tend to contain less naphtha material (having boiling points below 400°F) and less high-boiling-range material (having boiling points above 1000°F). As can be seen from Figure 25, the shale oil from the in situ retorting process of Occidental Petroleum tends to have a flatter distillation curve than the shale oils from the Paraho, Tosco, and Union surface retorting processes since it contains less naphtha and less heavy ends. According to Occidental, this is due to the mild coking the oil undergoes during retorting (McCarthy and Cha, 1976). The lower concentrations of naphtha and heavy ends in the in situ retorted oils also result in somewhat lower pour points, viscosities, and nitrogen contents.

The distillation curves of Figure 25 have been shown as bands, rather than lines, because slight changes in retorting conditions will produce variations in the boiling range. (The Lurgi curve is shown as a broken

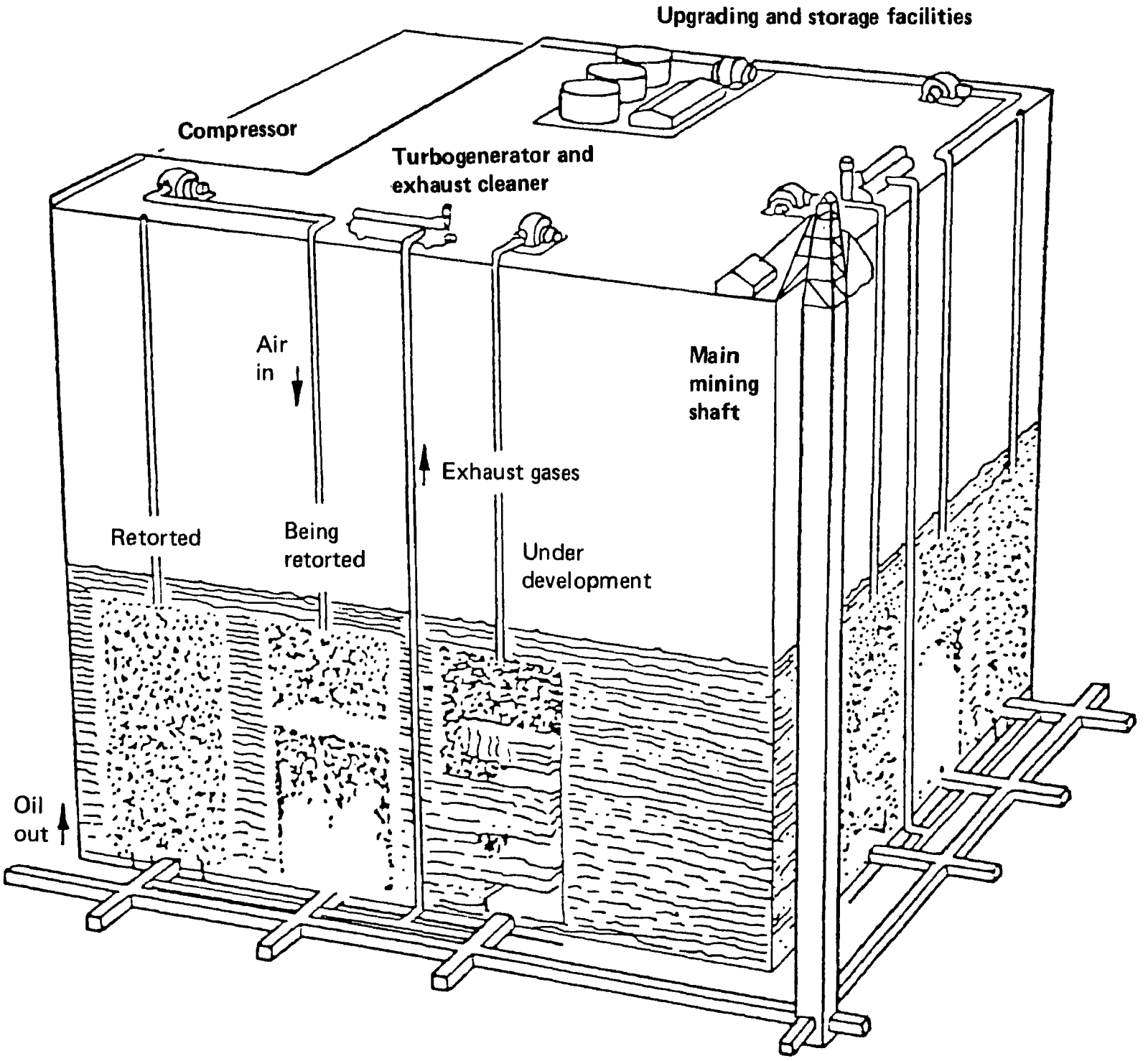


Figure 24 Lawrence Livermore Laboratory Rubble In Situ Extraction (RISE) process (Sladek, 1975)

Shale source	Colo	Colo	Colo	Colo	Utah	Utah	Colo	Colo	Utah
Grade, gallons per ton	--	--	28	28	32	32	--	36	33
Gravity, °API	18.6	22.7	22.8	21.2	21.4	20.2	21.5	22.2	22.8
Carbon, wt %	84.0	84.8	84.45	85.3	84.2	84.27	--	--	84.2
Hydrogen, wt %	12.0	11.61	11.55	11.15	11.7	11.68	--	--	11.4
Oxygen, wt %	0.9	0.9	0.94	1.12	1.51	1.23	--	0.9	--
Nitrogen, wt %									
Basic	--	--	--	1.04	--	1.26	--	--	--
Total	2.0	1.74	1.76	1.77	2.09	1.93	1.8	1.8	1.9
Sulfur, wt %	0.9	0.81	0.79	0.61	0.66	0.55	0.7	0.8	0.6
Hydrogen/carbon ratio	1.79	1.64	1.64	1.56	1.67	1.67	--	--	1.6
Ash, ppmw	--	50	600	300	4,400	3,000	--	--	1,40
Carbon residue, wt %	5.6[b]	--	1.7[b]	--	2.7	4.3[b]	1.8	2.1	2.0
Flash point, °F[c]	192[d]	79[d]	--	118	--	128	--	--	--
Pour point, °F	80	60	60	60	--	40	70	60	50
Visbreaking, ssu[e]									
100°F	210	98.2	--	136	150	165	--	--	190
210°F	--	--	--	--	--	42	--	--	--
Acid number, mg/g	--	--	--	2.6	--	4.0	--	--	--
Base number, mg/g	--	--	--	--	--	12.1	--	--	--
Nickel, ppmw	4	--	--	2.5	--	<2	--	--	--
Vanadium, ppmw	1.5	--	--	0.56	--	<20	--	--	--
Iron, ppmw	55	--	40	60	142	56	--	--	40
Copper, ppmw	--	--	--	11	--	<2	--	--	--
Arsenic, ppmw	--	--	50	52	45	49	--	50	37
Chloride, ppmw	--	--	5	--	--	15	--	--	--
Paraffins, ppmw	--	--	--	9	--	9	--	--	--
Olefins, ppmw	--	--	--	7	--	7	--	--	--
Naphthenes, ppmw	--	--	--	8	--	10	--	--	--
Aromatics, ppmw	--	--	--	48	--	45	--	--	--
Polar aromatics, ppmw	--	--	--	24	--	24	--	--	--
Carbon insolubles, ppmw	--	--	--	4	--	5	--	--	--
Distillation temperatures, °F									
IBP		139	120	145		152			176
10%	465	400	330	397		345			443
30%	640		551	660		633			666
50%	775	731	711	797		799			791
70%	980		848	903		919			891
90%		960	984	1037		1078			949
End point		1077	1100	1100		1100			1092

[a]Steam Gas Recirculation retort.

[b]Conradson carbon.

[c]Pensky-Martens, unless otherwise noted.

[d]Cleveland Open Cup.

	Utah	Colo	Colo	Colo	Colo	Colo	Colo	Colo	Colo
	19	--	35	--	--	--	--	--	--
	19.6	20.2	20.6	27.0	23.8	28.4	25.0	24.8	24.3
	84.21	83.13	85.1	85.2	85.9	--	--	--	84.86
	11.82	11.43	11.1	11.34	11.1	--	--	--	11.80
	1.89	1.16	1.2	1.15	1.17	--	--	1.03	--
7	1.19	--	1.1	--	--	--	--	--	--
6	2.09	2.18	1.9	1.65	1.72	1.41	1.3	1.58	1.50
4	0.5	0.66	0.7	0.66	0.75	0.72	0.64	0.74	0.71
9	1.69	1.64	1.56	1.59	1.50	--	--	--	1.67
	500[b]	3000	1000[b]	--	--	0.06	--	--	--
	3.1[b]	--	4.0[b]	--	3.86	1.7	--	--	--
	198	--	--	--	115	--	--	--	--
	75	90	80	--	65	40	50	--	65
	285	--	110	39	53	78	80	--	116
	45	44	38	--	--	--	--	--	--
	2.9	2.3	--	--	--	--	1.53	1.63	--
	13.6	38	--	--	--	--	--	--	--
	20	--	1.6[g]	--	4	--	--	--	--
22	<20	--	0.4[g]	--	5	--	--	--	--
0	140	70	40	--	--	--	--	--	--
3	<2	--	0.15[g]	--	--	--	--	--	--
3	19	28	21	--	10	--	--	--	--
	6	<0.2	10	--	--	--	--	--	--
7	7	10	--	--	--	--	--	--	--
3	5	6	--	--	--	--	--	--	--
1	10	8	--	--	--	--	--	--	--
3	44	46	--	--	--	--	--	--	--
9	29	23	--	--	--	--	--	--	--
1	5	6	--	--	--	--	--	--	--
5	220	886	80	--	158	--	250	204	--
2	503	608	340	230	320	--	465	450	475
0	690	659	525	420	457	--	575	540	600
4	827	776	720	605	619	--	670	616	685
2	952	871	885	770	777[h]	--	765	684	775
0	--	995	1035	950	842[h]	--	900[i]	742	915
0	1100	1022	1125	--	--	--	1050[i]	--	--

ybolt seconds, universal.

analyzed by Exxon; U, by Universal Oil Products, and O, by Occidental.

scher assay oil data.

80 percent.

95.5 percent.

Composition, wt %								
Carbon	84.27	84.54	83.20	83.82	84.31	84.81	85.20	84.21
Hydrogen	11.68	13.07	12.78	12.41	12.75	11.51	11.24	10.37
Oxygen	1.23	1.33[b]	1.99[b]	1.88	1.38	1.27	1.07	1.28
Nitrogen, basic	1.26	0.56[b]	1.06[b]	0.97	1.10	1.17	1.33	1.52
Nitrogen, total	1.93	0.23	0.85	1.34	1.39	2.04	2.15	3.25
Sulfur	0.55	0.62	0.54	0.71	0.76	0.52	0.46	0.42
Hydrogen/carbon ratio	1.66	1.86	1.84	1.78	1.81	1.63	1.58	1.48
PNOA by mass spectroscopy, vol %								
Paraffins		24.6	21.0					
Naphthenes		7.4	4.8					
Aliphatic monoolefins		31.0	33.1					
Cyclic monoolefins		13.7	11.1					
Alkylbenzenes		22.0	20.8					
Alkylindans + Tetralins		1.3	8.3					
Alkylnaphthalenes		0.0	0.9					
Structure by ASTM D-2007, wt %								
Paraffins	--	22.9[c]	19.3[c]	15.3	18.5	9.4	3.0	
Naphthenes	--	7.5[c]	4.9[c]	12.7	16.1	12.8	8.7	2.6
Monoolefins	--	43.5[c]	42.5[c]	10.4	2.2	2.3	3.5	
Aromatics	--	26.1[c]	33.3[c]	52.5	41.2	52.9	52.8	31.7
Polar aromatics	--	--	--	8.7	21.3	21.8	32.0	38.7
Pentane insolubles	1.5	--	--	0.4	0.7	0.8	0.0	27.0
CHONS, within a boiling fraction, wt %								
Pentane insolubles	79.05							
Carbon	79.05							
Hydrogen	7.80							
Oxygen	6.78[d]							
Nitrogen, total	5.71							
Sulfur	0.66							
Polar aromatics								
Carbon				78.90	82.21	81.96	82.94	
Hydrogen				10.05	9.86	10.14	10.34	
Oxygen				5.50	3.61	2.52	2.27	
Nitrogen, total				5.25	4.13	4.50	3.83	
Sulfur				0.30	0.22	0.32	0.26	
Total acid number, mg/g	4.0	4.0	7.9	6.5	2.8	--	--	--
Total base number, mg/g	12.1	15.8	24.2	26.0	37.1	--	--	--
Chloride, ppm	15	18	--	--	6	--	--	--

[a]Whole oil structure (percent by weight): 9 paraffins, 10 naphthenes, 7 monoolefins, 45 aromatics, 24 polar aromatics, 5 pentane insolubles.

[b]Problems with the test.

[c]Estimated wt % by PNOA-MS, not ASTM D-2007.

[d]By difference.

Source: McCarthy and Cha (1976).

	Whole oil[a]	IBP-375°F	375-425°F	425-500°F	500-650°F	650-850°F	850-1050°F	1050°F+
Composition, wt %								
Carbon	84.21	83.89	83.88	84.34	83.29	84.12	84.40	84.41
Hydrogen	11.82	12.98	12.25	12.41	11.83	11.43	11.16	10.13
Oxygen	1.89	1.67[b]	2.20[b]	2.05	1.92	1.52	1.43	2.06
Nitrogen, basic	1.19	1.03[b]	1.20[b]	0.99	1.14	1.25	1.58	
Nitrogen, total	2.09	0.94	0.94	1.06	1.74	1.99	2.35	2.73
Sulfur	0.50	0.37	0.46	0.51	0.47	0.58	0.37	0.30
Hydrogen/carbon ratio	1.68	1.86	1.75	1.77	1.70	1.63	1.59	1.44
PNOA by mass spectroscopy, vol %								
Paraffins		19.5	19.8					
Naphthenes		6.2	6.2					
Aliphatic monoolefins		31.0	24.2					
Cyclic monoolefins		14.9	11.0					
Alkylbenzenes		26.1	28.4					
Alkylindans + Tetralins		2.2	8.5					
Alkylnaphthalenes		0.1	1.9					
Structure by ASTM D-2007, wt %								
Paraffins	--	18.0[c]	17.9[c]	15.9	14.8	9.5	3.3	
Naphthenes	--	6.2[c]	6.2[c]	11.4	10.0	16.4	11.2	2.1
Monoolefins	--	44.3[c]	33.4[c]	11.2	6.4	1.6	2.7	
Aromatics	--	31.5[c]	42.5[c]	49.3	50.4	49.7	50.2	26.8
Polar aromatics	--	--	--	11.9	17.7	22.3	31.8	52.3
Pentane insolubles	0.7	--	--	0.3	0.7	0.5	0.8	18.8
CHONS, within a boiling fraction, wt %								
Pentane insolubles								
Carbon	76.65							
Hydrogen	7.13							
Oxygen	10.42[d]							
Nitrogen, total	5.29							
Sulfur	0.51							
Polar aromatics								
Carbon				78.23	81.08	82.30	83.56	
Hydrogen				9.81	10.28	9.98	10.24	
Oxygen				5.83	3.16	2.42	1.45	
Nitrogen, total				5.61	5.01	4.57	3.96	
Sulfur				0.21	0.22	0.36	0.35	
Total acid number, mg/g	2.9	3.1	4.3	4.7	3.3	--	--	--
Total base number, mg/g	13.6	24.7	30.0	31.0	37.4	--	--	--
Arsenic, ppm	19	12	6	6	14	16	19	27
Chloride, ppm	6	14	--	--	--	--	--	--

[a]Whole oil structure (weight percent): 7 paraffins, 10 naphthenes, 5 monoolefins, 44 aromatics, 29 polar aromatics, 5 pentane insolubles.

[b]Problems with the test.

[c]Estimated wt % by PNOA-MS, not ASTM D-2007.

[d]By difference.

Source: McCarthy and Cha (1976).

Process/ composition	Boiling range			
Tosco[a]	IBP-170°F	170-310°F	310-375°F	375-640°F
Aromatics	4.0	15.0	23.5	47.5
Olefins	63.0	55.5	49.0	37.0
Saturates	33.0	29.5	27.5	15.5
Paraffins	28.0	22.2	20.2	-
Cyclo paraffins	4.8	7.2	7.3	-
Di-cyclo paraffins	0.2	0.1	0.0	-
Occidental[b]		IBP-375°F		375-500°F
Position in shale oil		0.2-2.4		2.4-14.2
Paraffins		26		
Olefins		21		
Naphthenes		4		
Aromatics[c]		49		
FIA analysis[d]				
Paraffins and naphthenes				43.8
Olefins				22.7
Aromatics				33.5

[a]C. W. Waitman of Tosco Corp., personal communication to J. O. Berga, November 16, 1977.

[b]R. D. Ridley of Occidental Oil Shale, Inc., personal communication to J. O. Berga, November 21, 1977.

[c]Oxygen, nitrogen, and sulfur compounds included with aromatics.

[d]Fluorescent indicator adsorption.

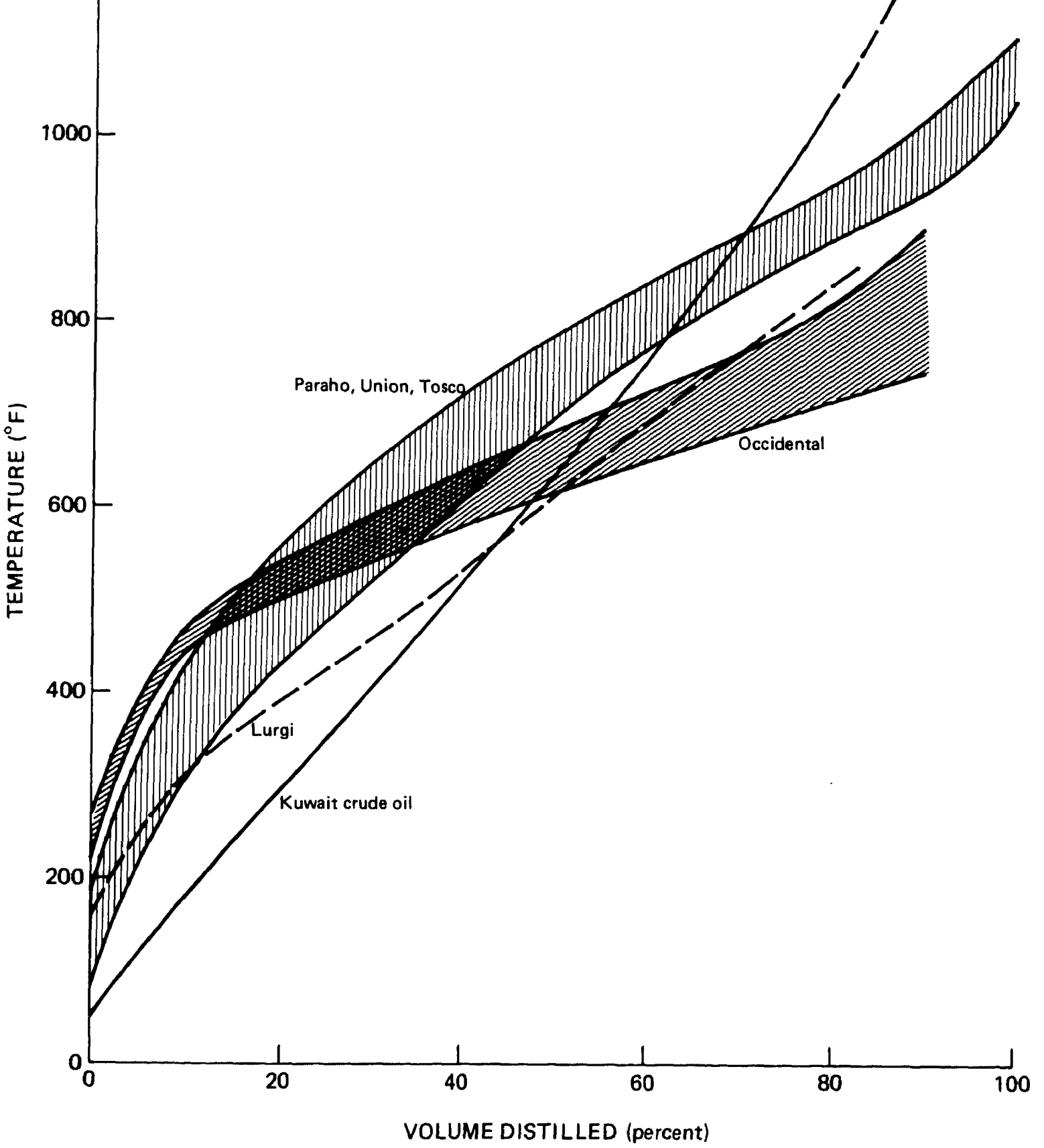


Figure 25 Distillation curves of shale oils

One of the most significant characteristics of raw shale oil is the high nitrogen content. The distribution of nitrogen and sulfur over the boiling range is shown in Figure 26. The nitrogen content of raw shale oil increases as distillation progresses, as does that of petroleum crude oil, but this is not true of the sulfur content. The concentration of sulfur in the raw shale oil reaches a peak at the 10 percent point and then decreases as distillation continues.

Although the metal concentrations in raw shale oil are lower than those in petroleum crude, there are a number of other trace elements that present difficulties. The most significant of these is arsenic, which, along with nitrogen, is discussed in greater detail below. In fixed bed hydrotreating, the fine shale rock particles in the raw shale oil (known as "fines" or "ash") present additional problems, plugging the catalyst beds and increasing the pressure drops in the system; to deal with this particular problem, de-ashing will be necessary, either as a separate step or as part of the de-arseniting process.

The limited data available show that raw shale oils from all retorting processes studied have similar chemical structures, which are significantly different from those of petroleum crudes. In general, the shale oils are lower in paraffins, higher in olefins, and higher in aromatics and polar aromatics.

In raw shale oils, the lower boiling fractions tend to have higher concentrations of paraffins and olefins and lower concentrations of aromatics than the higher boiling fractions (Figure 27). The naphthene content tends to remain fairly constant across the boiling range.

The high percentage of polar aromatics in the higher boiling range fractions indicates the presence of nitrogen, oxygen, and sulfur in the ring structure of the higher molecular weight aromatics, and the data bear this out. This characteristic increases the difficulty of denitrifying shale oil to levels that are acceptable for processing into transport fuels.

The significance of the nitrogen, arsenic, sulfur, and oxygen contents in the refining of raw shale oil are discussed below.

Nitrogen

The predominant nitrogen compounds in raw shale oils are pyridines, pyrroles, quinolines, and nitriles (Burger et al., 1975). The basicity of these and other nitrogen compounds found in raw shale oils has been reported previously (Poulson et al., 1976).

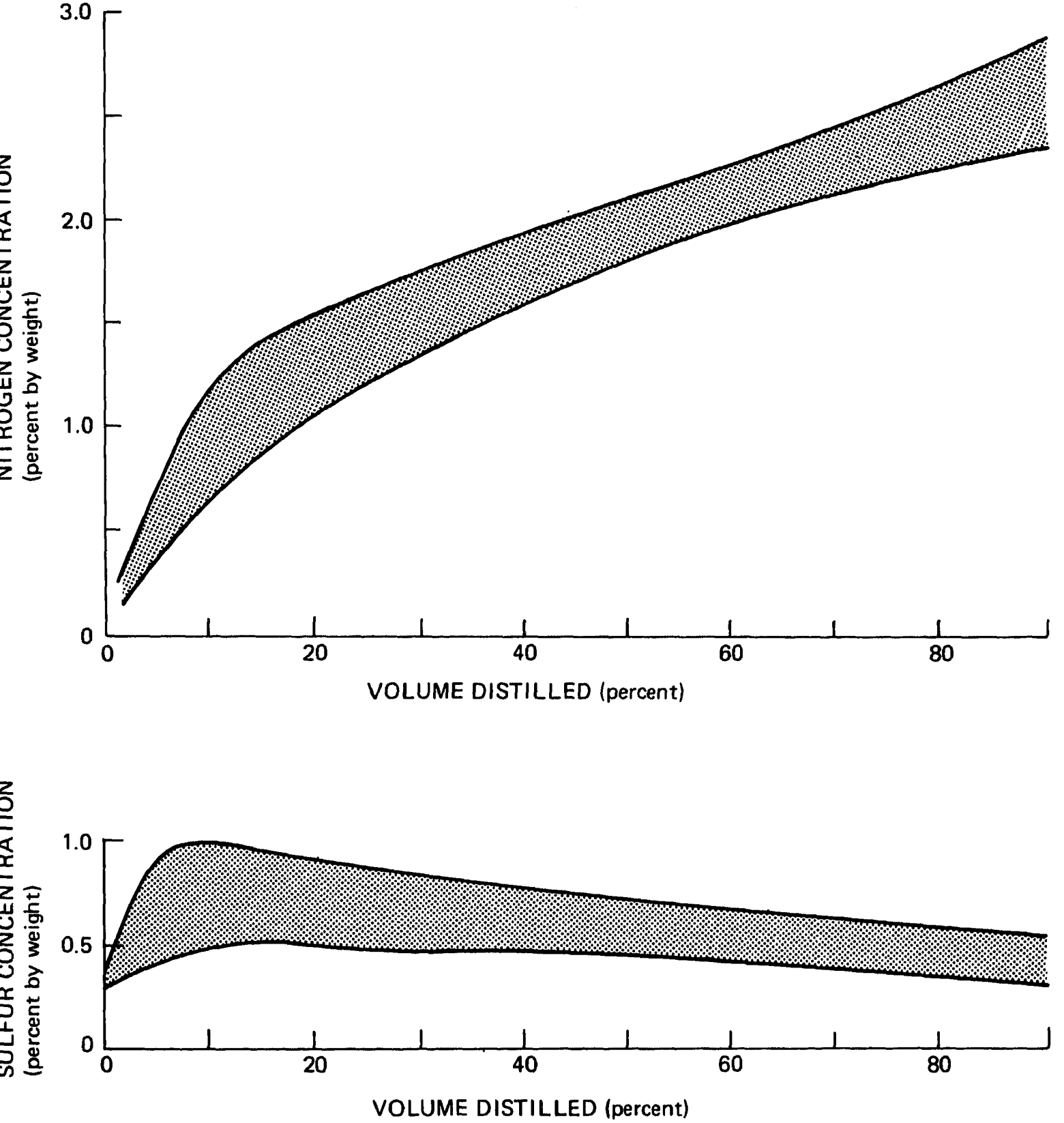


Figure 26 Nitrogen and sulfur concentrations in raw shale oil, as a function of distillation range (Lovell, 1978)

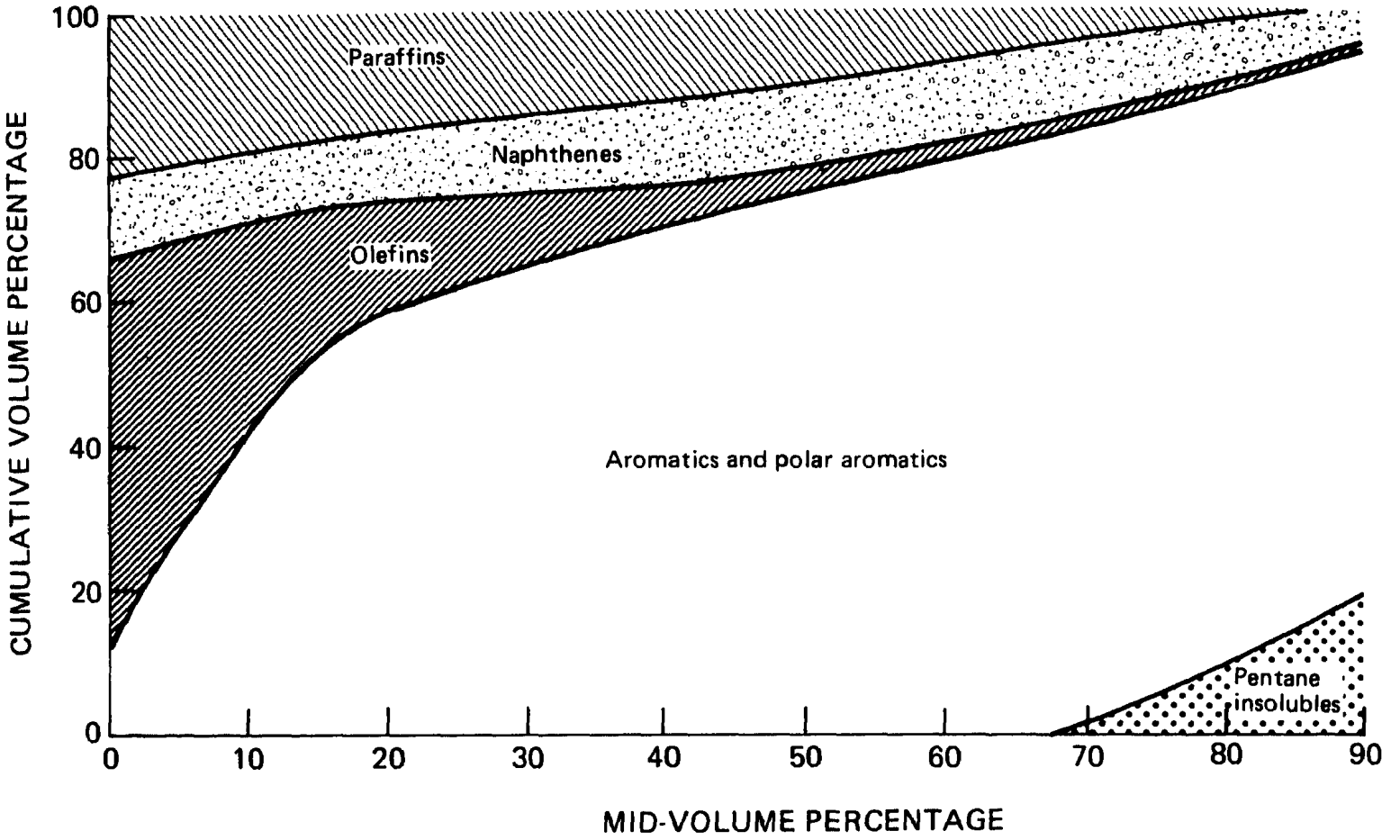


Figure 27 Chemical structure of raw shale oil (Lovell, 1978)

ally contain somewhat lower concentrations of heteroatom and polar compounds than surface-retorted oils (Poulson et al., 1976) but the concentrations are still much higher than those in conventional crude oils. A significant degree of upgrading (denitrification) will be necessary with all raw shale oils before they can be refined to useful end products by conventional processes.

Removing the nitrogen from raw shale oil is critical because of its effect on downstream processing. Direct fixed-bed hydrogenation of both whole and fractionated raw shale oil has been used for nitrogen reduction (Sullivan and Stangeland, 1978), and results to date support the conclusion that hydrodenitrification of whole shale oil to the ppm range is feasible. The process conditions required would be more severe than those of present refining operations, however; high pressures ($\geq$2000 psi) and high hydrogen consumptions ($\geq$2000 standard cubic feet per barrel) would be necessary to reach the desired nitrogen levels. Although this is technically feasible, the costs would be high.

Another possible approach to nitrogen removal is to combine hydroprocessing of the raw shale oil with an acid extraction step to reduce the nitrogen compounds by precipitation.[a] Relatively mild hydroprocessing conditions can bring about a substantial conversion of neutral and acidic nitrogen compounds to basic amines that can then be converted into insoluble amine salts with a strong acid (e.g., HCl).

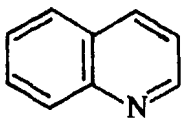
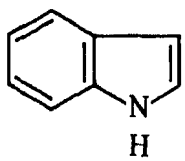
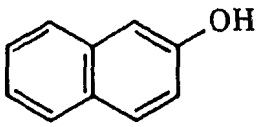
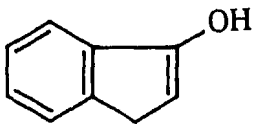
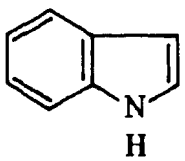
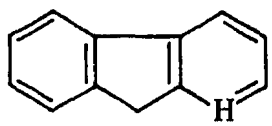
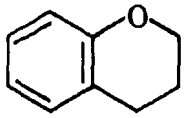
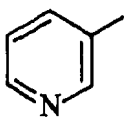
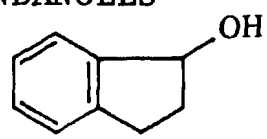
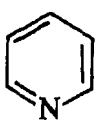
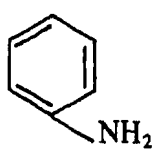
There is a need for more research on such mechanisms together with process research and development on nitrogen removal using catalyst selectivity, solvent extraction (acid treating), and hydroprocessing.

Arsenic

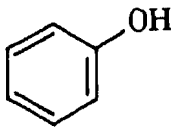
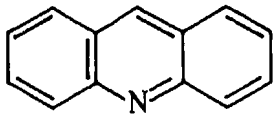
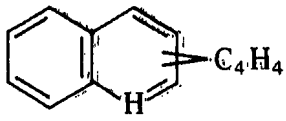
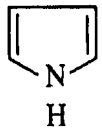
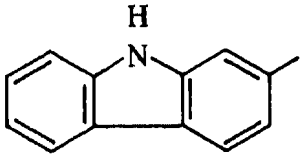
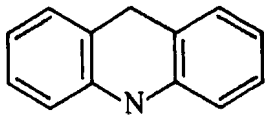
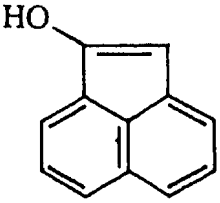
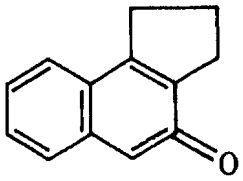
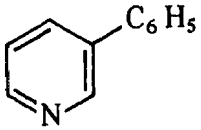
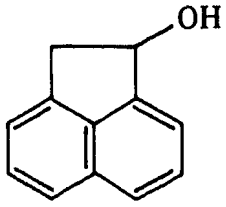
The concentration of arsenic in raw shale oil is on the order of 1000 times higher than the concentration of arsenic in conventional crude oil. Green River oil shale has an arsenic content of about 50 ppm (Burger et al., 1975), and comparable levels have been found in shale oils recovered elsewhere by various retorting processes. Since arsenic poisons certain catalysts currently used for refining oil, most of the arsenic in shale oil must be removed before it is piped into a conventional refinery. Generally speaking, it is desirable to reduce the level of arsenic in the naphtha fraction charge to 5 ppb or less before catalytic reforming. The distribution of arsenic throughout the boiling range of raw shale oils is most likely due to the presence of various species of molecular arsenic.

---

[a] [illegible], personal communication.

	Union B			Paraho DH		
	425-500°F	500-650°F	650-850°F	425-500°F	500-650°F	650-850°F
QUINOLINES 	M	M	M	M	L	M
CYCLOALKYLINDOLES 						
NAPHTHOLS 	T	M	M	T	M	S
INDENOLS 						
INDOLES 	M	L	M	M	L	S
INDENO-PYRIDINES 						
CHROMANS 	S	M	S	S	S	S
CYCLOALKYLPYRIDINES 	M	M	M	M	M	M
INDANOLES 	M	M	M	S	M	M
PYRIDINES 	M	M	M	M	S	M
ANILINES 						

L: large; M: medium; S: small; T: trace

	Union B			Paraho DH		
	425-500°F	500-650°F	650-850°F	425-500°F	500-650°F	650-850°F
PHENOLS 	L	S	M	L	S	S
ACRIDINES  BENZOQUINOLINES 	M	S	M	S	S	M
DIHYDROXYPHENOLS CATECHOL RESORCINAL QUINOL FURANS PYROLES 	S	S	S	S	S	S
ALKYLCARBAZOLES  ACRIDANS 	S	S	L	S	S	L
ACENAPHTHYLENOLS  BENZINDANONES 	S	S	M	T	T	M
PHENYL-PYRIDINES 	S	M	M	T	M	M
ACENAPHTHENOLS 	T	S	S	T	S	S

Arsenic is a very difficult element to identify analytically, and the imbalances that frequently occur in fractional versus whole oil determinations are difficult to explain. Some arsenic compounds may be thermally unstable and volatilize overhead. All in all, very little is known about the nature of arsenic compounds in raw shale oil. More research needs to be done in this area.

As has already been noted, part of the arsenic in raw shale oil is contained in the fines, or ash. Care should be used in drawing inferences from the ash content figures reported in Table 20, however, since it is not known if they were obtained from the different retorting processes in comparable ways. It is highly probable, in any event, that de-ashing to about 10 ppm (maximum) will be required where fixed-bed catalytic processing (e.g., hydrotreating) is to be used as the initial upgrading step. In some instances, de-ashing may take place during the de-arseniting step. Several de-arseniting processes are currently available for licensing from Union Oil, Arco, and others (Burger et al., 1975), but the removal of arsenic requires additional research.

Sulfur

Sulfur concentrations in raw shale oils are in the range of 0.6-0.7 percent by weight, the distribution being fairly flat across the boiling range, as seen in Figure 26. (The sulfur concentrations in the lighter fractions of raw shale oil are slightly higher than those in the lighter fractions of petroleum crude oils.) Since sulfur is removed by hydroprocessing more easily than nitrogen, the denitrification of raw shale oil to a satisfactorily low level will also reduce the sulfur content to an acceptable level.

Oxygen

The oxygen content of raw shale oil is about 1.0-1.5 percent by weight, higher than the oxygen content of most petroleum crudes, although some California crudes have oxygen concentrations close to this level. The oxygen content is not expected to cause any unusual problems during the processing of shale oils into transportation fuels.

BIBLIOGRAPHY

Aspegren, O. E. A. 1952. Heat Treatment of Piece-Shaped Material. U.S. Patent 2,872,386.

Petroleum Chemistry Preprint 20, no. 4, pp. 765-775. Washington, D. C.: American Chemical Society.

Cameron Engineers, Inc. 1975. Synthetic Fuels Data Handbook. Denver, Colo.: Cameron Engineers.

Dockter, L. 1978. Lecture notes, 3rd In Situ Energy Recovery Technology Short Course, University of New Mexico, Albuquerque, June 2.

Duir, J. H., R. F. Deering, and H. R. Jackson. 1977. Continuous Upflow Retort Improves Shale Processing. Hydrocarbon Processing 56(5):147-150.

Hartley, F. L. 1958. Progress Report on Oil Shale Retorting and Refining. Independent Petroleum Association of America Monthly, August, pp. 23-24. Washington, D.C.: Independent Petroluem Association of America.

_____. 1974. Oil Shale: Another Source of Oil for the United States. Paper presented at Oil Daily's Third Annual Synthetic Energy Forum, New York, June 10. (Available from Union Oil Company of California, Corporate Communications Department, Box 7600, Los Angeles, Calif. 90051.)

Hartley, F. L., and G. H. Hemmen. 1957. Oil Shale Mining and Retorting Methods. Mining Congress Journal 47(1):60-62.

Hopkins, J. M., H. C. Huffman, A. E. Kelley, and J. R. Pownell. 1976. Oil Shale Retorting Technology of Union Oil Company of California. Paper No. 6/3-C, presented at 81st National Meeting, American Institute of Chemical Engineers, Kansas City, Mo., April 11-14. (Available from American Institute of Chemical Engineers, 345 E. 47th Street, New York, N. Y. 10017.)

Lovell, P. F. 1978. Production of Utah Shale Oil by the Paraho DH and Union "B" Retorting Processes. Proceedings of 11th Oil Shale Symposium, pp. 184-192. Golden, Colo.: Colorado School of Mines Press.

McCarthy, H. E., and C. Y. Cha. 1976. The Oxy-Modified In Situ Oil Process Development and Update. Proceedings of 9th Oil Shale Symposium. Quarterly of the Colorado School of Mines 71(4):85-100.

Poulson, R. E., C. M. Frost, and H. B. Jensen. 1976. Characteristics of Synthetic Crude from Crude Shale Oil Produced by In Situ Combustion Retorting. Advances in Chemistry Series, ed. T. F. Yen, Vol. 151, pp. 1-10. Washington, D.C.: American Chemical Society.

Rammler, R. W. 1969. The Distillation of Fine-Grained Oil Shale by the

Sass, A., and R. E. Lumpkin. 1977. In Situ Processing of Oil Shale. Paper presented at 106th Annual Meeting, American Institute of Mining, Metallurgical and Petroleum Engineers, Atlanta, March 6-10. (Available from Mr. Allen Sass, The Occidental Research Corporation, 1855 Carrion Road, LaVerne, Calif. 91750.)

Schora, F. C., P. B. Tarman, and H. L. Feldkirchner. 1976. Oil Shale--Present Technology and the IGT/AGA Process. Proceedings of the 8th Synthetic Pipeline Gas Symposium, pp. 281-314. Sponsored by the American Gas Association, Energy Research and Development Administration, and International Gas Union. Arlington, Va.: American Gas Association.

Sladek, T. A. 1975. Recent Trends in Oil Shale--Part 2: Mining and Shale Oil Extraction Processes. Colorado School of Mines Mineral Industries Bulletin 18(1):1-20.

Sullivan, R. F., and B. E. Stangeland. 1978. Catalytic Hydroprocessing of Shale Oil to Produce Distillate Fuels. American Chemical Society Division of Petroleum Chemistry Preprint 23, no. 1, pp. 322-342. Washington, D. C.: American Chemical Society.

Superior Oil Company. 1977. Multi-Mineral Oil Shale Project Venture Summary. Houston, Tex.: Superior Oil.

6 REFINING OF COAL AND SHALE LIQUIDS

The refining of coal and shale liquids will require many of the processing steps now used in refining petroleum. The types, sizes, and numbers of processing units needed, however, will depend on the properties of the feedstocks and the desired product slates. The feedstocks, in turn, will vary with the coal liquefaction or shale retorting process used.

Shale oils extracted by different processes, in fact, do not differ radically from one another, but coal liquids vary widely from process to process. Pyrolysis, for example, yields highly unsaturated liquids containing high-boiling-point tarry fractions contaminated with coal solids. Direct liquefaction without the addition of catalysts produces high-boiling-point solvent-refined coal that may also be contaminated with solids. Catalytic hydroliquefaction can produce either an all-distillate synthetic crude oil or a liquid containing high-boiling-point fractions and nondistillable material that may contain solids. Indirect liquefaction via synthesis gas yields all-distillate liquids or methanol, both quite different in character from direct liquefaction products. Table 25 lists, for several coal, shale, and petroleum liquids, the characteristics that determine the requirements of refining.

Large-scale pilot plant tests of shale retorting have been carried out for many years, yielding relatively large amounts of liquids for evaluation, and studies of the refining characteristics of shale oil have been carried out in considerable detail. Experimentation with coal liquids, on the other hand, has been much more recent and only relatively small quantities of the product have been available. Thus, while it is possible to present some quantitative data on shale oil refining, the refining of coal liquids must be handled in a more qualitative manner.

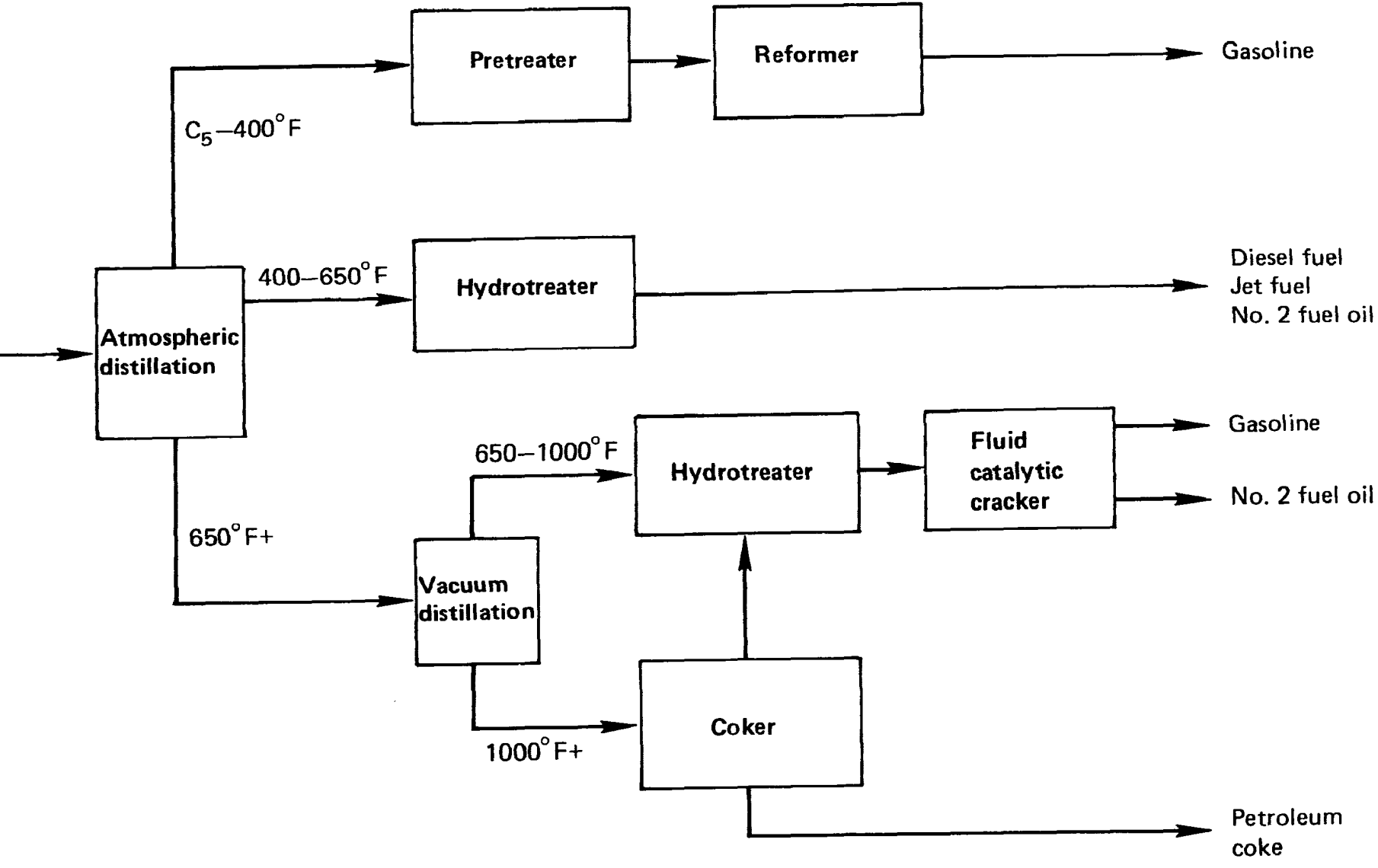
For reference purposes, Figure 28 is a simplified schematic diagram of a typical sour crude refinery, with the gas processing steps omitted. The relative size and severity of treatment in the various process units vary, of course, with the sulfur content and boiling range of the crude as well as the desired product slate.

	SRC product	H-Coal	Synthoil	COED product
Composition				
Carbon, wt %	87.93	89.00	87.62	83.05
Hydrogen, wt %	5.72	7.94	7.97	8.35
Oxygen, wt %	3.50	2.12	2.08	7.15
Nitrogen, wt %	1.71	0.77	0.97	1.10
Sulfur, wt %	0.57	0.42	0.43	0.35
Nickel, ppmw	2	1	1	1
Vanadium, ppmw	7	3	2	7
Titanium, ppmw	130	80	150	1
Iron, ppmw	140	20	375	350
Kinematic viscosity, cSt at 100°C	Solid	318	28.6	1090
Pour point, °C	Solid	50	4	50
Type of coal used	High volatile (Illinois No. 6)	High volatile bituminous (Illinois No. 6)	High volatile bituminous (Pittsburgh seam)	High volatile bituminous
Reference	Callen et al. (1976)	Callen et al. (1976)	Callen et al. (1976)	Johns et al. (1972)

[a]In another West Texas vacuum residue (not the one described by Callen et al

CFFC Product	Paraho Shale Oil Colo. 28	El Palito No. 6 Fuel Oil	540 C West Texas Sour Residuum
88.4	84.5	86.4	83.88
7.0	11.2	11.2	9.97
1.5	1.6	0.3	0.48
0.69	1.96	0.41	0.4[a]
0.25	0.64	1.96	4.19
1	3.5	59	34[a]
1	0.2	275	52[a]
9.5	--	78	--
57	100	6	--
71[b]	177	--	--
--	72	--	--
Bituminous (Illinois No. 6)			
Sze (1980)	Table 19	Callen et al. (1976)	Callen et al. (1976)

the fraction boiling above 975°F had these metal contents (Sze, 1980).



gure 28 Flow diagram of typical sour crude refinery, omitting gas processing steps

Heavy Liquid Feedstocks Containing Nondistillable Materials

Typical of the heavy liquid feedstocks obtained from coal are (a) solvent-refined coal (SRC), (b) catalytically hydroliquefied coal liquids containing nondistillable fractions, and (c) pyrolysis liquids.

As has already been noted in this report, the most effective way of using these heavy liquids at first may be to replace the petroleum fractions now being used for boiler fuels with coal-derived liquids that have undergone a minimum of refining. The petroleum fractions now used in boilers could then be refined to lighter products. This scheme would probably be cheaper than refining the coal liquids to lighter products. If coal liquids are put through a mild to moderate hydrotreating step to stabilize them and remove sulfur and nitrogen, the product will be usable not only as an environmentally acceptable boiler fuel but also as a refinery feed, as discussed below.

If, on the other hand, it is transportation fuels that are required, the refining could be carried out as shown in the schematic block flow diagram of Figure 29. The object of this processing sequence is to maximize the production of transportation fuels at the lowest practical level of hydrogen consumption. For heavy SRC-like feedstocks and the COED raw pyrolysis liquids, a liquid fluidized-bed front-end hydrocracking process such as LC-Fining or H-Oil could be used. If a fixed-bed mode of contacting is used, the particulate content of these liquids (0.1-0.2 percent by weight) will cause premature fouling or clogging of the catalyst bed. The relatively high residue contents of these two feedstocks require the use of front-end hydrocracking, which is more readily carried out with all-distillate syncrude-type feedstocks, as described further on.

In the first processing step of the refinery in Figure 29, the raw pyrolysis liquid or molten (or fluxed) heavy coal-derived liquid such as SRC would be mixed with recycle oil and fed to a liquid fluidized-bed hydrocracker containing a sulfur- and nitrogen-resistant catalyst. The objective of this step would be to reduce the fraction boiling over 850°F in the feed, to increase the H/C atomic ratio, and to remove a substantial amount of the heteroatoms (S, N, O). Hydrocrackate or effluent product from this step would then be atmospherically distilled into a full-range naphtha, an atmospheric gas oil, and atmospheric bottoms products. Following this, the atmospheric bottoms would be vacuum distilled into a vacuum gas-oil product and a vacuum bottoms product (boiling at more than about 900°F). The latter could be fed either to a hydrogen plant converting steam and carbonaceous feedstocks into hydrogen via a partial oxidation process, or to a coker. The product slate from the coker would consist of a coker gas oil, coke, and minor amounts of coker naphtha and gas. Whether coking were desirable would depend on the amount of additional liquid it would produce. The coke

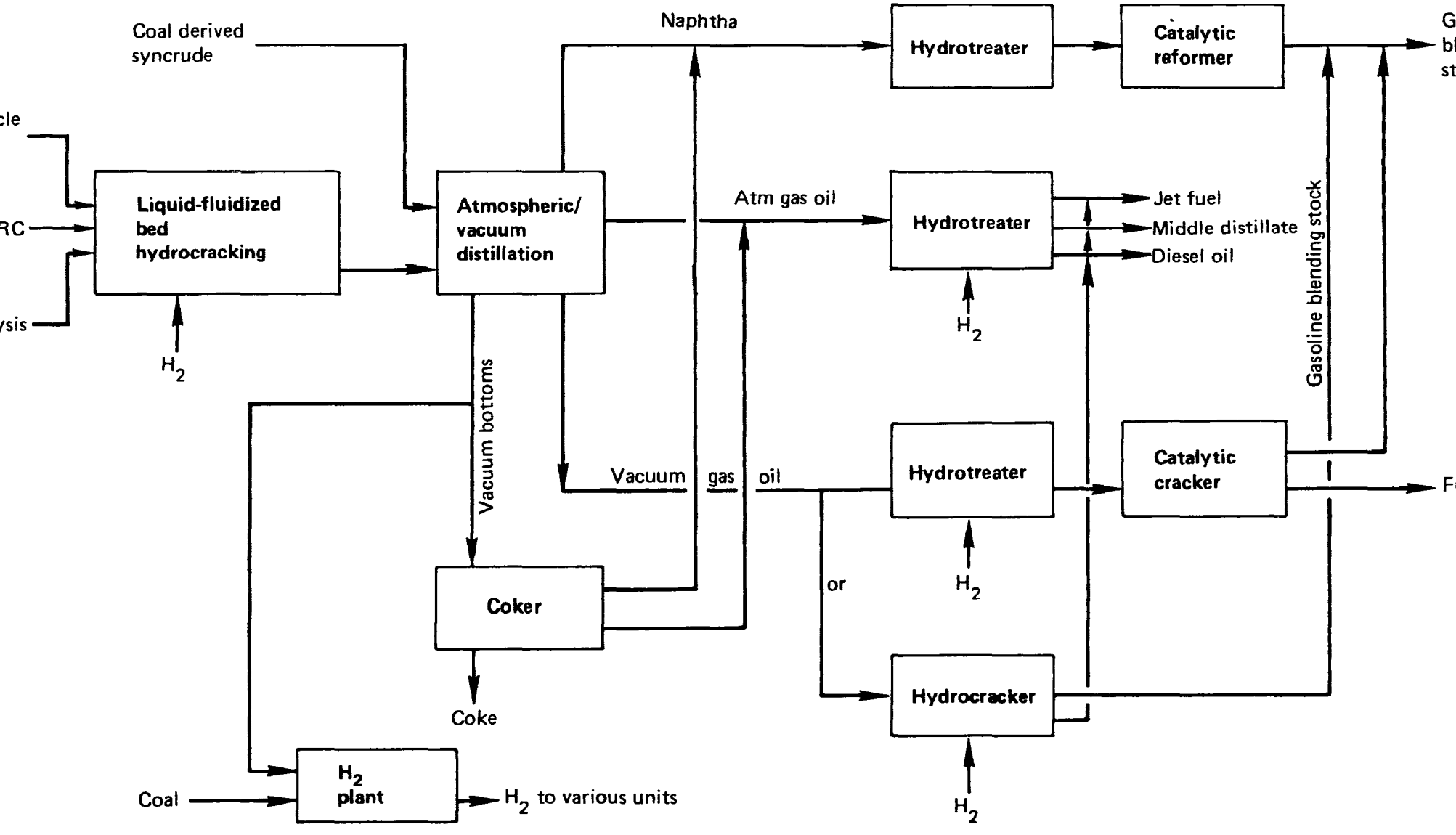


Figure 29 Coal liquid refining steps for producing transportation fuels

o reduce the sulfur and nitrogen contents, a step normally carried out rior to conventional catalytic reforming with noble metal catalysts. atalytic reforming would increase the aromatic content and octane number f the hydrotreated naphtha feedstock and yield a net hydrogen make. The roduct of the reforming would be a uniquely suited gasoline blending tock.

The atmospheric gas oil generated by the atmospheric distillation ould be combined with coker gas oil, if available, and fed to a hydro-reater where the H/C ratio would be increased, the feedstock aromatic ontent decreased, and the heteroatoms content also decreased. If suffi-ient hydrogen were added and the aromatic content sufficiently reduced both goals expensive to realize), the products would be usable as jet uels and diesel oils. Less hydrogen would be required to produce mid-distillate heating oils.

The vacuum gas oil prepared during the vacuum operation could also e hydrotreated and then catalytically cracked. This combination of steps would produce both gasoline and fuel oil. The vacuum gas oil naterial could, on the other hand, be hydrocracked to produce a product slate of gasoline, jet fuels, mid-distillates, and diesel fuels. The gasoline so produced might or might not require reforming, depending on the pool octane requirement.

This refining scheme will require a hydrogen plant. The heavy vacuum still bottoms would probably be a convenient feed for hydrogen production; if additional hydrogen were required, it could be obtained by the partial oxidation of additional coal.

All-Distillate Synthetic Crudes from Direct Liquefaction

All-distillate synthetic crudes obtained by direct coal liquefaction are lighter (i.e., have a lower boiling range) than the heavy coal liquids and are free of particulate contaminants. As a result, the refining of such feedstocks for the production of gasoline and heating oil is relatively straightforward. As indicated in the block flow diagram of Figure 29, these syncrudes can be processed without the front-end hydrocracking step. If, however, they have a significant concentration of diolefins and require substantially lower temperatures in the primary distillation steps to avoid coking, it may prove advantageous to subject them first to a mild hydrotreating to improve their stability. The addition of this step would reduce the severity of the hydrotreating required downstream.

The following fractions may be obtained from the atmospheric and vacuum distillation units: a light naphtha cut, a heavy naphtha frac-

either hydrotreated and catalytically cracked or hydrocracked. There would be no need for a coker to process any heavy residue.

Refining all-distillate crudes is simpler because of the more severe hydroliquefaction used to produce them. It is too soon, however, to generalize on whether it would be more economical to produce and ship an SRC or an all-distillate syncrude from a primary liquefaction plant. The economics certainly favor the production of the maximum liquid product with minimum overall hydrogen consumption.

Indirectly Produced Coal-Derived Liquids

Indirectly produced coal-derived liquids (e.g., Fischer-Tropsch liquids methanol, gasoline derived from methanol) are characterized by their lower boiling ranges and the essentially complete absence of combined sulfur and nitrogen, a result of the elaborately purified syngas (H_2 and CO) used in the production of these liquids. Although the refining of these indirectly produced liquids was not considered within the scop of this study, a few fundamental facts should be noted:

- Fischer-Tropsch liquids contain straight-chain olefins and paraffins, with almost no aromatics. Diesel fuels are easier to produce from them than from the highly aromatic products of direct liquefaction. The gasoline boiling range fraction has a low octane rating, requiring octane improvement processing steps (e.g., catalytic reforming of the naphtha and isomerization of the C_5/C_6 fractions).

- Gasoline from methanol contains aromatics and has a higher octane rating than Fischer-Tropsch liquids. The process produces in addition LPG and small amounts of fuel gas, and almost no materials with boiling points above that of gasoline.

REFINING SHALE LIQUIDS

Raw shale oil may have to be subjected to either visbreaking or mild hydroprocessing at the retorting site (depending on the retorting process) to improve its handling characteristics and reduce its pour point before it is sent to a refinery. It is not expected, in general, that the refining would be carried out at the retorting site. Figure 30 shows the various processing alternatives, with the product slate and product quality dictating the viable options. For a particular sit ation studied, the yields and product qualities of the shale oil after processing by the various options indicated in Figure 30 are as given in Table 26. In this study, the light ends were used internally for

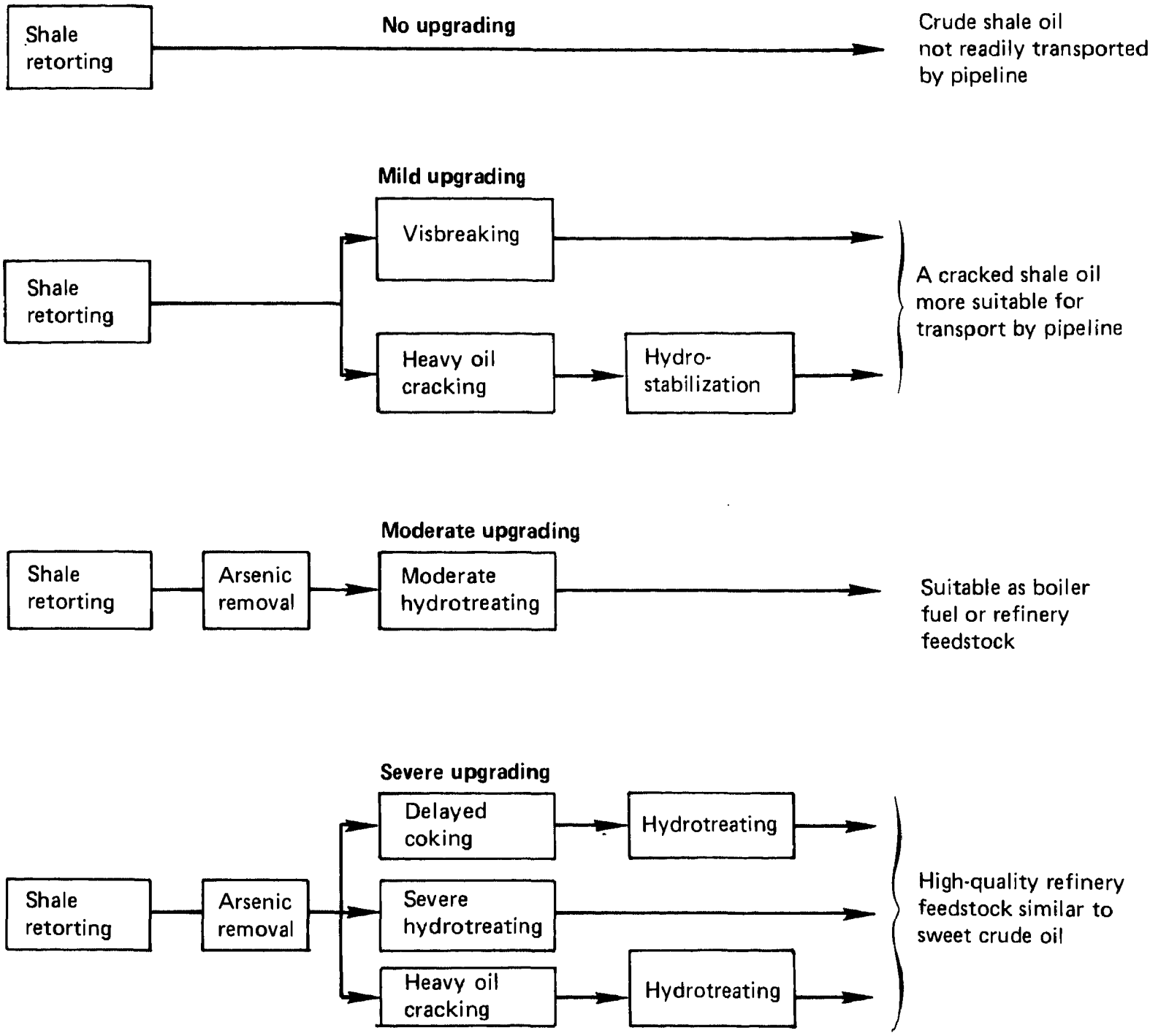


Figure 30 Processing alternatives for shale liquids according to quality of end product

TABLE 26 Oil shale facility process summary (based on 100,000 barrels per calendar day crude shale oil)

	Crude shale oil	Visbreaking	Heavy oil cracking/ hydro-stabilization
C_4+ liquid oil product recovered, barrels per calendar day	100,000	100,300	88,920[a]
Heating value of oil recovered, 10^9 Btu per calendar day	605	605	490
Shale oil product quality			
Gravity, °API	19.8	20.4	34.0
Pour point, °F	85.0	20.0	35.0
Viscosity, cSt at			
40°F	460[e]	370	8
100°F	45	35	3
Reid vapor pressure, psi	3.5[f]	1.0	7.0
C_5-430°F			
Volume, percent	7.0	11.2[f]	37.7
Sulfur, ppmw	8,000	9,200	5,400
Nitrogen, ppmw	5,000	10,000	7,000
430-600°F			
Volume, percent	16.0	21.8[f]	22.5
Sulfur, ppmw	7,000	6,400	7,700
Nitrogen, ppmw	14,000	16,500	21,000
600-1050°F			
Volume, percent	70.0	61.0	34.3
Sulfur, ppmw	6,300	5,800	5,700
Nitrogen, ppmw	24,100	23,500	26,000
1050°F+			
Volume, percent	7.0	6.0	5.5
Sulfur, ppmw	--	--	--
Nitrogen, ppmw	--	--	--
Total			
Volume, percent	100.0	100.0	100.0
Sulfur, ppmw	7,000	6,700	5,800
Nitrogen, ppmw	21,000	20,300	17,200

[a]Shale oil product has 5.5 percent C_4 by volume.

Boiler fuel	Refined shale oil	coking	hydro-treating	cracking/ hydro-treating
96,000	96,000	88,000[b]	87,020[c]	87,930[d]
581	568	508	506	500
36.3	40.0	29.7	43.0	43.0
60.0	50.0	35.0	35.0	35.0
20[e]	13[e]	20	8.5	8
5.5	4	5	3.3	3
1.0	1.0	3.0	1.5	5.0
16.5[f]	23.6[f]	21.1[f]	29.1	40.1
50	-	10,000	1	1
400	1	10,000	1	1
29.7[f]	32.0[f]	32.2[f]	39.1	31.5
--	50	8,500	20	20
--	200	16,000	200	200
49.4	40.0	45.0	31.6	25.3
600	500	6,000	20	20
2,500	600	21,000	1000	200
4.4	4.4	--	--	--
--	--	--	--	--
--	--	--	--	--
100.0	100.0	100.0	100.0	100.0
500	250	7,000	15	13
2,200	340	18,000	410	385

[d]Shale oil product has 3.1 percent C_4 by volume.

[e]With addition of pour depressant.

[f]400°F TBP cut point.

Arsenic removal is generally carried out in an atmosphere of hydrogen under pressure at intermediate temperatures (450-600°F) in a fixed bed; a disposable adsorbent catalytically promotes the deposition of the arsenic in much the same way that other metals are deposited on hydroprocessing catalysts. The cost of satisfactory removal is currently estimated to range from 25 to 50 cents per barrel. The panel believes that much more research is needed into the nature of the arsenic compounds in shale oils, possible mechanisms and better materials for removing these compounds, and better methods for disposing of the spent adsorbent.

As shown in Figure 30, a moderate hydrotreating of shale oil will yield environmentally acceptable boiler fuels and suitable refinery feedstocks. Direct hydrogenation at moderate pressures (1000-1500 psig) will reduce the nitrogen and sulfur contents of shale oils to the point at which they can probably be burned in boilers and process heaters without exceeding the emissions standards for SO_x and NO_x. Moderately hydrotreated shale oil could also be admixed with crude fractions being used in various refinery processes.

It may be desirable to upgrade the shale oil even more, producing a synthetic crude that is compatible with conventional crudes, allowing it to be mixed with petroleum-based streams in existing refineries. This upgrading can be accomplished in several ways, the principal methods being (a) coking plus hydrotreating of the coker distillates, (b) severe hydrotreating of full-boiling-range raw shale oil, and (c) heavy oil cracking followed by hydrotreating. Let us examine these three alternatives briefly:

(a) Where coking plus hydrotreating of the coker distillates is employed, the primary problems are handling the high-nitrogen coke produced (about 4 percent N) as well as low liquid yields. The coke could be gasified to produce hydrogen but the economics of all the options would need to be carefully examined because of the low liquid yields (see Table 26).

(b) Severe hydrotreating of full-boiling-range raw shale oil may be the most attractive processing route for shale oil, since it provides the greatest flexibility in the choice of the final product slate and the least severe environmental problems. As indicated in a Chevron study (Sullivan and Stangeland, 1978), acceptable catalyst life can be achieved and fully acceptable feedstock quality produced for downstream refining (e.g., catalytic cracking and reforming). The Chevron study shows the optimal product nitrogen level to be about 500 ppm; the conditions required to achieve this level are the following: a pressure of about 2200 psig (1850 psia H_2 partial pressure)

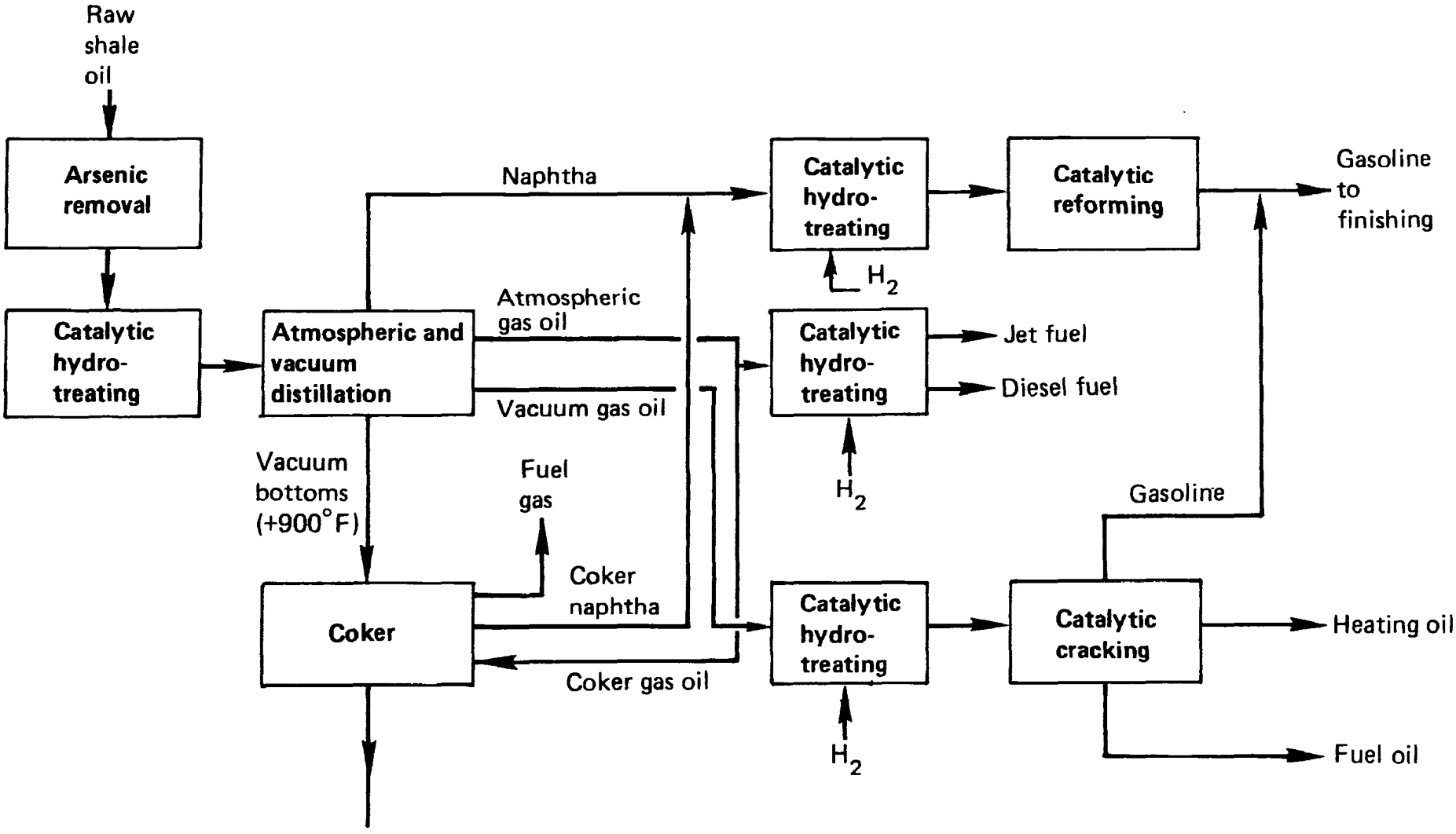
ponding increases in paraffin and naphthene contents. The resulting naphtha cut is a better feedstock for reforming than is found in most petroleum crudes.

(c) The third processing alternative for producing high-quality refinery feedstock is the use of heavy oil cracking (HOC-fluid catalytic cracking technology licensed by Phillips/Kellogg), followed by hydrotreating of the cracked naphtha, light gas oil, and heavy gas oil in separate units. Since the coke produced is far in excess of that required to maintain a heat balance, a very considerable amount of high pressure steam is generated, requiring efficient utilization. This process is similar to that of (a) above, but coke is not obtained as a product; instead, the coke is burned in the regenerator, the heat recovery being in the form of high pressure steam. As with the process described in (a), the product requires reasonably severe hydrotreating for nitrogen removal.

The processing route that is optimal will depend on whether the refining takes place at the mine site as an integral part of the total mining-retorting-upgrading process, in a separate new refinery specifically designed for this purpose, or at an existing refinery to which facilities for handling shale oil are added. Many factors must be taken into account in choosing the location, including the total energy balance, the availability of feed streams for hydrogen generation, and the desired product mix. There are additional factors, such as the availability of water, the labor pool, the availability of space for expansion, and the means for transporting raw materials and products.

Figure 31 is a process chart for a fully integrated raw shale refinery designed to maximize the production of transportation fuels with the minimum use of hydrogen. After arsenic removal and hydrotreating, the shale oil feedstock is atmospherically distilled into a full-range naphtha, an atmospheric gas oil cut, and an atmospheric bottoms product that is subsequently vacuum distilled into a vacuum gas oil fraction and a vacuum bottoms product ($900^{\circ}F+$). If the vacuum bottoms product is large, it could be fed to a coking process step or, alternatively, to a solvent de-asphalting process step that produces a decarbonized oil and/or asphaltic residuum that could be used for the generation of hydrogen in a partial oxidation process. If the feedstock has not been sufficiently hydrotreated, the de-asphalted oil would be fed to a hydrotreater and then catalytically cracked.

If the atmospheric residuum does not contain too large a quantity of heavy material or asphaltenes, the entire atmospheric residuum can be charged to a hydrotreater and catalytic cracker.



gure 31 Shale oil refining steps to produce transportation fuels with minimum use of hydroge

yields are desired, fluid coking could be considered. In either case, coke might be used to produce fuel gas or hydrogen by partial oxidation, although flexicoking (a combination of fluid coking and partial oxidation) may provide another option.

Coker naphtha and straight-run naphtha from the atmospheric distillation could be combined and hydrotreated to produce a low-sulfur (less than 5 ppm), low-nitrogen (less than 1 ppm) naphtha suitable for catalytic reforming. For octane improvement, conventional catalytic reforming would be entirely satisfactory.

Atmospheric gas oil obtained from the initial atmospheric distillation operation could be combined with coker gas oil and put through a hydrotreating step to remove heteroatoms and saturate aromatic rings, yielding jet and diesel fuels.

Straight-run vacuum gas oil could be hydrotreated to reduce the concentrations of nitrogen, sulfur, and polynuclear aromatics prior to catalytic cracking. (If a de-asphalting process option is used, the decarbonized oil would be combined with the straight-run vacuum gas oil before it is hydrotreated.) The product slate from this part of the refinery would consist of gasoline, heating oil, fuel oil, and gas.

Another alternative processing strategy would be to eliminate the coker and substitute a hydrocracking process step for (or combine it with) the catalytic hydrotreating and catcracking combination, as shown in Figure 32. Hydrocracking should increase the quantities of naphtha and/or diesel and jet fuel produced, but the naphtha from the process would require catalytic reforming. If a sufficiently nitrogen-resistant hydrocracking catalyst is not available, nitrogen would have to be removed prior to hydrocracking in a hydrotreatment step.

REFINING TECHNOLOGY FOR CATALYTIC HYDROPROCESSING

Overview

Catalytic hydroprocessing should be given the greatest attention in future research efforts because of its importance in the refining of shale oil and direct-route coal liquids. It is essential for the removal of heteroatoms (particularly nitrogen and sulfur, which are present in large concentrations), and for the cracking of the high-molecular-weight coal liquids to more usable fractions.

While one of the major concerns with petroleum has been the sulfur in the crude, there are problems with nitrogen as well in coal and shale liquids because of increasing restrictions on NO_x emissions from fuels

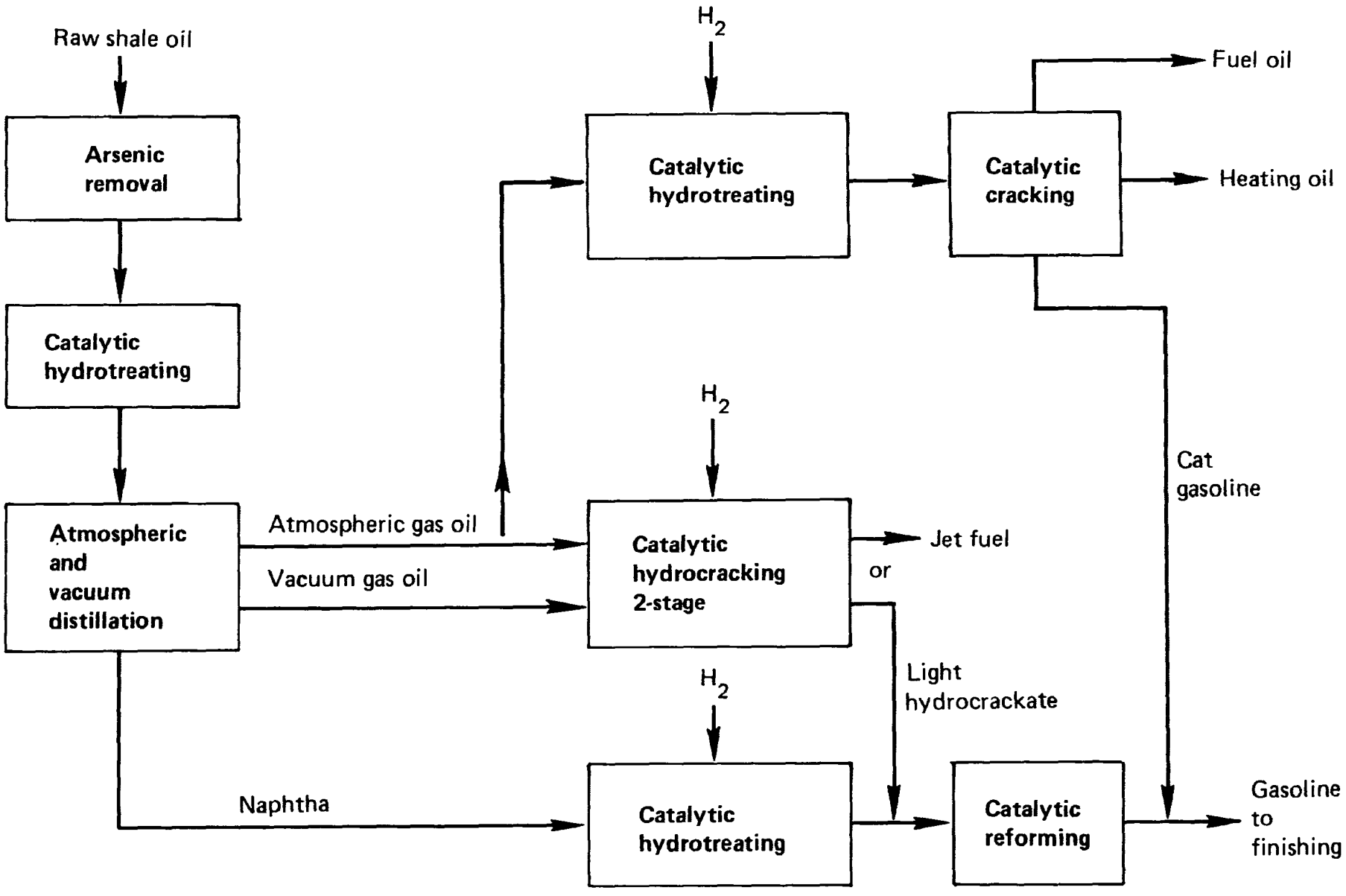


Figure 32 Shale oil refinery using substitute hydrocracking process step

molecular sieve catalyst during hydrocracking. The 100°F temperature increase required to maintain constant product quality results in a severe increase in the rate of catalyst deactivation and a corresponding reduction in catalyst life.

In practice, the removal of nitrogen is generally more difficult than the removal of sulfur. Table 27 shows the extent to which nitrogen and sulfur can be removed by hydroprocessing from a shale oil, solvent refined coal, Synthoil (a coal-derived liquid from an earlier process), and three different petroleum distillates. The figures show that a lower percentage of the nitrogen is removed, generally, even when the hydroprocessing removes a high percentage of sulfur.

As the boiling point of the feedstock increases, a given degree of sulfur and nitrogen removal requires a progressively higher severity (i.e., higher temperature, pressure, or hydrogen recycle rate, or lower space velocity), and may result in a shortened catalyst life.

The need for increasing the severity of the operating conditions with the boiling point of the feedstock results from several factors. In the higher-molecular-weight feedstock:

- The compounds from which the heteroatoms are to be removed are less reactive.
- The more highly aromatic molecules of the feedstock compete with the heteroatom-containing molecules for catalyst sites, reducing their rate of reaction.
- The more highly aromatic molecules deactivate catalysts more severely, requiring higher hydrogen pressures to reduce coke formation to an acceptable level.

The higher aromaticities of coal and shale liquids make them more difficult to hydrocrack and require a higher hydrogen consumption.

Catalysts

Typical catalysts for the processes described here consist of combinations of cobalt, nickel, molybdenum, and tungsten supported on alumina. Such catalysts are normally 3-6 percent cobalt or nickel and 12-18 percent molybdenum or tungsten. Under operating conditions, these metals are in the form of sulfides on the alumina. The preferred catalyst for hydrodesulfurization is Co-Mo/Al_2O_3 (cobalt molybdate on Al_2O_3). The frequent choice for hydrodenitrogenation is Ni-Mo or NiW on Al_2O_3. The preferred catalyst for hydrocracking is Ni and W on an acidic support

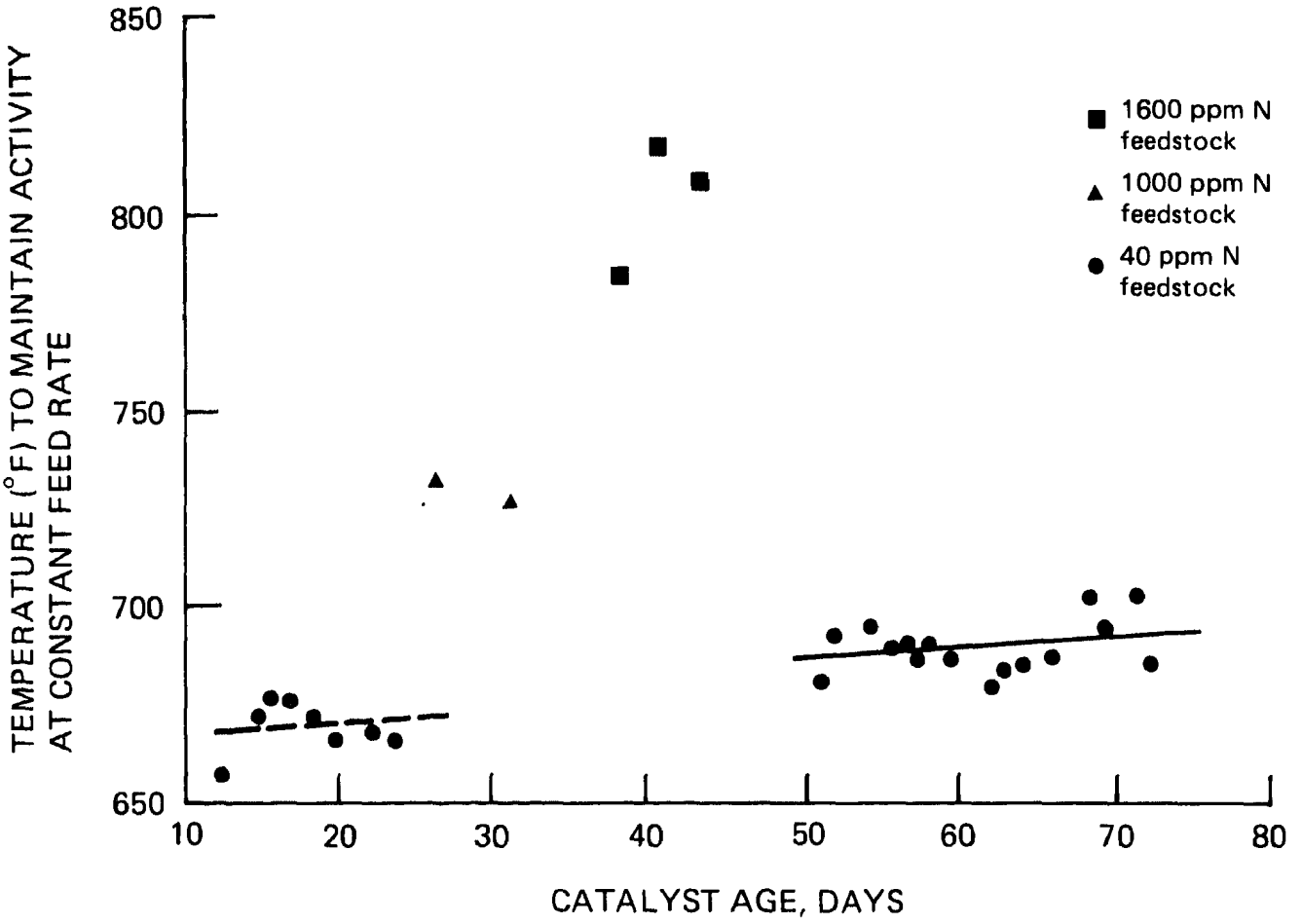


Figure 33 Effects of nitrogen content of feed on noble metal acid molecular-sieve catalyst in Unicracking-JHC process (Retallick, 1964)

weight

	Sulfur			Nitrogen		
	In original	In product	Percent removed	In original	In product	Percent removed
Shale oil[a]	0.6	0.0025	99.6	2.2	0.07	97
Solvent-Refined Coal II[b]	0.29	0.001	99.6	0.85	0.05	94
H-Coal[c]	0.32	0.001	99.6	0.46	0.014	70
Three petroleum distillates[d]	0.8	0.05	94	0.015	0.007	53
	1.19	0.07	94	0.056	0.041	27
	1.58	0.14	91	0.012	0.007	42

[a]Sullivan et al. (1977).

[b]Sullivan et al. (1980).

[c]Using Illinois No. 6 coal.

[d]Thomas (1970).

Any of these will catalyze all three reactions but with different selectivities. The best hydrogenation catalyst is probably Ni-W/Al_2O_3 but hydrocracking may also be catalyzed by nonacidic catalysts with an active hydrogenation-dehydrogenation component. Such catalysts, using a thermal cracking mechanism, are frequently preferred for very heavy feedstocks that would severely coke a strongly acidic support. For clean feeds, hydrocracking catalysts made up of a zeolite base with palladium or platinum are also employed (Ward, 1973).

Catalysts are generally extrudates. The particle size (1.5-3mm) is usually made as small as possible to minimize intraparticle mass transfer limitations, particularly for heavy feedstocks. The lower limit of particle size is set by the pressure drop allowable in the catalyst bed. Liquid fluidized-bed reactors have the advantage of

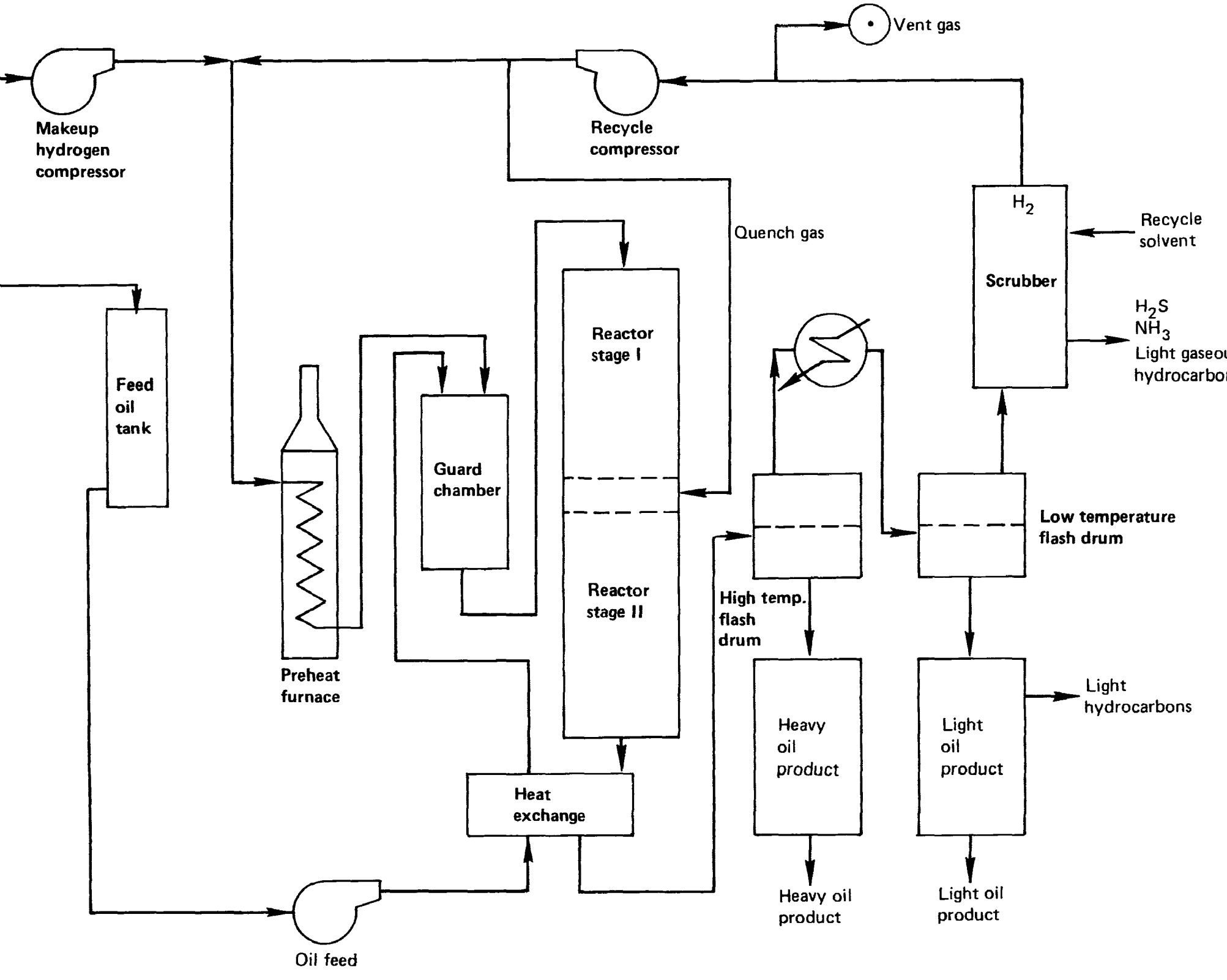
For petroleum feedstocks that are free of solids, the reactors used are generally the trickle-bed type, with the oil "trickling" down over the catalyst in the presence of high-pressure hydrogen.

With heavy coal or shale liquids that are contaminated with solids, liquid fluidized-bed reactors (e.g., LC-Fining or H-Oil reactors) must be used to avoid plugging. This type of reactor (essentially a stirred tank reactor) has the added advantage of permitting the intermittent addition of fresh catalyst and withdrawal of spent catalyst while the unit is on stream. It also allows the use of smaller catalyst particles (less than 0.8 mm), reducing the mass transfer problem encountered with heavier feeds. The greater volume requirement of this type of reactor can be largely offset by operating at higher average temperatures but the increased hydrocracking that results may be undesirable. The design of both reactor types is straightfoward because of the considerable experience gained from the petroleum industry. What are needed are the catalyst deactivation rates with the feedstocks to be used. In operation, the reactor temperature can be increased with time to compensate for the deactivation of the catalyst and maintain constant conversion. If the deactivation is due to coking, the catalyst can be regenerated by controlled combustion of the coke. If, however, the deactivation of the catalyst is due to the deposition of metals, regeneration will not be possible.

Catalyst costs for processes that involve direct contact between coal and a particulate catalyst may be as high as $1.00 per barrel, but the cost may be much lower when solids separation is carried out prior to hydroprocessing.

Reactor systems include a preheat furnace, reactor, hydrogen recycle and purification system, and product separation train (Figures 34 and 35). For dirty feeds, the life of the catalyst can be extended by first passing the feed through a guard chamber with a cheap disposable catalyst to remove metals and rapid-coking components.

For the more severe operations with coal and shale liquids that would lead to undesirably high temperatures in the catalyst bed (hydrogenation and hydrocracking being quite exothermic), trickle-bed reactors are staged and cold gaseous hydrogen injected between the stages to reduce the temperature of the reactant stream. When two stages are necessary (because the feed is high in nitrogen and sulfur and particularly heavy, and considerable hydrocracking is required), more efficient process operation can be achieved by placing each stage in its own recycle loop. By this means, NH_3 and H_2S can be separated from the hydrogen before it is fed to the second catalyst bed (Figure 35). With the removal of sulfur and nitrogen in the first stage, hydrocracking can be carried out more effectively in the second stage.


Vent gas
Makeup hydrogen compressor
Recycle compressor
Quench gas
H_2
Scrubber
Recycle solvent
H_2S
NH_3
Light gaseou
hydrocarbo
Feed oil tank
Reactor stage I
Guard chamber
Preheat furnace
Reactor stage II
High temp. flash drum
Low temperature flash drum
Heat exchange
Heavy oil product
Light oil product
Light hydrocarbons
Heavy oil product
Light oil product
Oil feed

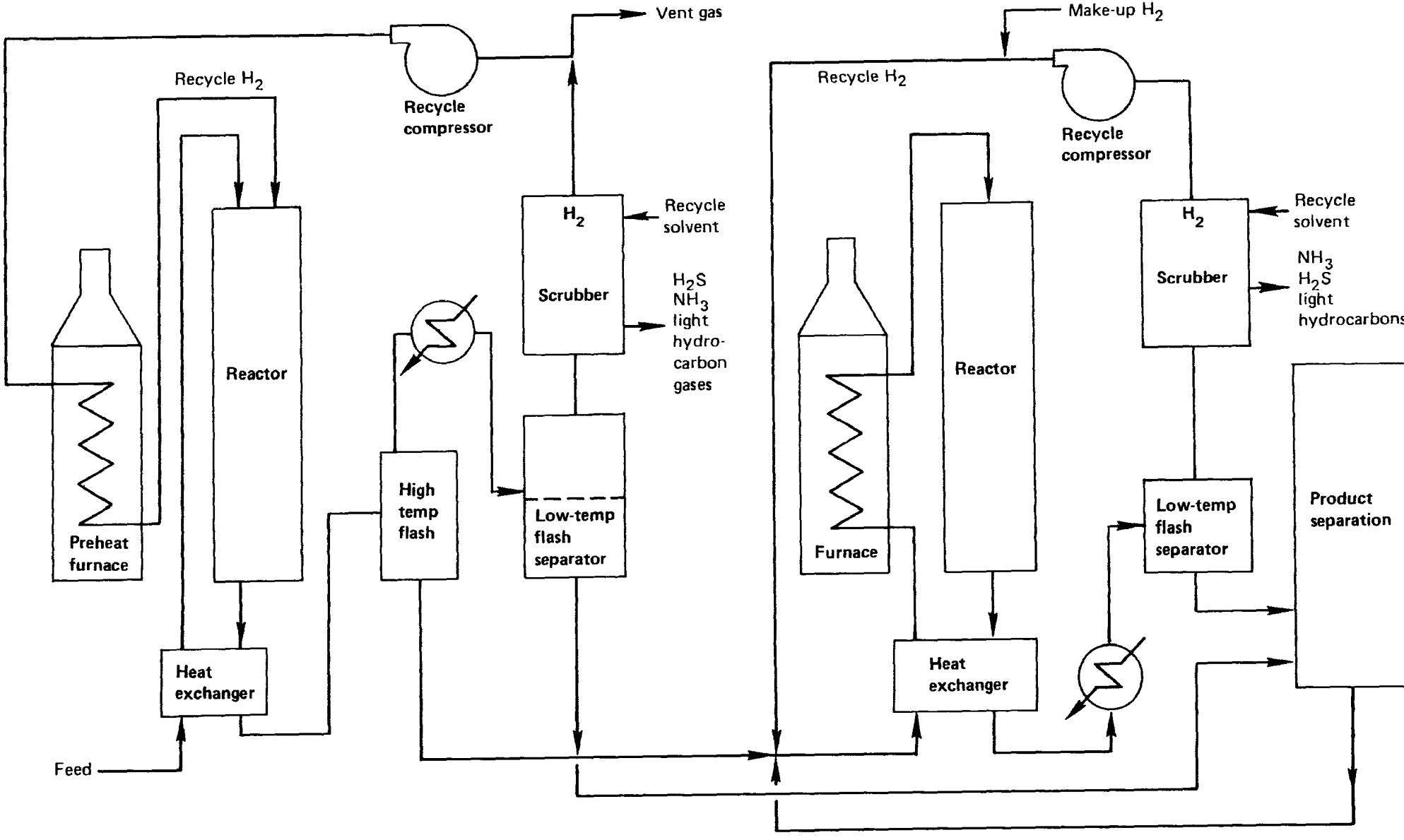


Figure 35 Two-stage hydroprocess-hydrotreating system, with parallel recycle loops for h

CONCLUSIONS

The conclusions reached on the processing of coal and shale liquids are as follows:

- Since shale liquids are more nearly like petroleum than are coal-derived liquids, shale liquids are more easily processed to diesel and jet fuels. Minimally upgraded shale oil could initially enter the market as a boiler fuel or refinery feedstock.

- If coal and shale liquids can be transported economically, they could be refined in existing refineries, suitably modified, without requiring the construction of new ones.

- The refining of coal and shale liquids will involve many of the processing steps used in petroleum refining, although they may vary in some detail. Refineries for processing coal and shale liquids will, consequently, resemble modern petroleum refineries.

- The most important step in refining coal and shale liquids is hydroprocessing to remove the heteroatoms (S, N, O), reduce the average molecular weight to that required for the products being produced, and reduce the aromaticity. In shale liquids, high hydrogen consumption during hydrodenitrogenation makes nitrogen removal the single most important problem in refining. In coal liquids, high hydrogen consumption is required to reach acceptable nitrogen contents and to reduce the aromatic content.

- Hydrogen consumption represents a major fraction of the cost of processing coal and shale liquids, and needs to be minimized.

- Coal and shale liquids can be hydroprocessed with the use of catalysts, as is done at present with petroleum. The lighter fractions of coal and shale liquids, behaving much like light petroleum feeds, can be hydroprocessed and refined with existing technology, requiring little further research. But fractions of coal and shale liquids require more severe hydroprocessing than the corresponding petroleum fractions and cause more severe catalyst deactivation. They also require more hydrogen. Particular attention must be given to the development of catalysts that can remove nitrogen with less hydrogen consumption. Catalysts with greater activity maintenance are also needed.

- Hydroprocessing costs are increased by the severity of the processing conditions. The costs can be reduced by using coal and shale liquids of better quality.

tents of coal-derived liquids are much lower and pose no proble

- After coal and shale liquids have been adequately hydroprocesse they generally can be processed in much the same way as petrole feed stocks. Since the refining technology for petroleum has been so well developed, a major R&D effort is not needed on downstream processes for coal and shale liquids (i.e., catalyti cracking, catalytic reforming, isomerization, etc.).

RECOMMENDATIONS

- Although some processes for refining coal and shale liquids are already available, the costs are still high, due primarily to t high rate of hydrogen consumption required at present for boiling point reduction and the removal of sulfur and nitrogen heteroatoms. A reduction in the cost of hydrogen should therefore be an important objective of research and development efforts.

- The lighter components of coal and shale liquids after refining could be used initially as gasoline blending agents.

- Research and development should be carried out on the refining (particularly the hydroprocessing) of liquids with a wide range of properties. None of the three routes for direct coal liquefaction (i.e., pyrolysis, solvent extraction, and catalytic liquefaction) can, as yet, be considered out of the running. Each has its advantages and each produces liquid products with different properties.

- A fundamental research program is required for a better understanding of hydrodenitrogenation catalysis and the development of improved and new catalysts. The Department of Energy should actively sponsor such a program. Also needed are a better understanding of the forms of arsenic and mineral matter in coa and shale liquids and better ways of removing these catalyst poisons.

- The Department of Energy should continue its program of sponsoring tests of industrial proprietary processes to keep abreast of the current state of the art.

- The Department of Energy should sponsor considerably more fundamental research on the reactions involved in the refining of coal and shale liquids. A better understanding of the reaction mechanisms is essential to the development of new and improved processes.

end-use equipment. Facilities should be established for the supply of adequate quantities of fuels with a wide range of compositions for testing and research in fuel-consuming devices. Full cooperation with the fuel and equipment manufacturing industries is essential.

BIBLIOGRAPHY

Callen, R. B., J. G. Bendoraitis, A. V. Cabal, T. R. Stein, and S. E. Voltz. 1976. Upgrading of Coal Liquids for Use as Power Generation Fuels. Phase 1 report, pp. 34-35. Springfield, Va.: National Technical Information Service (PB-252-939, EPRI-361-1).

Crynes, B. L. 1977. Catalysts for Upgrading Coal-Derived Liquids. Quarterly report no. 7, Table 4. Norman, Okla.: University of Oklahoma (Department of Energy contract FE2011).

Johns, J. J., J. F. Jones, and B. D. McMunn. 1972. Hydrogenated COED Oil. Proceedings: American Chemical Society 163rd National Meeting, Division of Fuel Chemistry, Vol. 16, no. 1, pp. 26-35. Washington, D.C.: American Chemical Society.

Retallick, W. B. 1964. Hydroprocesses. In Kirk Othmer Encyclopedia, 2d ed., Vol. 2, p. 427. New York: John Wiley and Sons, Interscience Publishers.

Sze, M. C. 1980. Personal communication.

Sullivan, R. F., H. A. Frumkin, C. E. Rudy, and H. C. Chen. 1977. Refining and Upgrading Synfuels from Coal and Oil Shales by Advanced Catalytic Processes. Quarterly report, April-June 1977. Washington, D.C.: U.S. Department of Energy (Energy Research and Development Administration contract EF-76-C-01-2315).

Sullivan, R. F., D. J. O'Rear, D. E. Stangeland, and H. A. Frumkin. 1980. Refining of Syncrudes. Paper presented at 45th Midyear Refining Meeting of the American Petroleum Institute, Houston, Tex., May 15.

Sullivan, R. F., and B. E. Stangeland. 1978. Catalytic Hydroprocessing of Shale Oil to Produce Distillate Fuels. American Chemical Society Division of Petroleum Chemistry Preprint 23, no. 1, pp. 322-342. Washington, D.C.: American Chemical Society.

Thomas, C. L. 1970. Catalytic Processes and Proven Catalysts. p. 160. New York: Academic Press.

Unicracking--JHC Hydrocracking Catalysts and Processes." New Advances
Proceedings--Division of Refining, Vol. 53, pp. 129-137. Washington,
D.C.: American Petroleum Institute.

7 HYDROGEN PRODUCTION

The preceding chapters have emphasized the importance of reducing hydrogen consumption in the conversion of coal to liquids meeting normal product specifications. Liquefaction plus subsequent refining might typically require about 6,000-9,000 cubic feet of hydrogen per barrel of refined products. Since the production of hydrogen from coal costs approximately $3 per thousand cubic feet (Cart et al., 1978), the cost of hydrogen will obviously be a major component of the total product cost. The incentive for producing hydrogen more cheaply is clearly great. A projection of the hydrogen demand for conventional uses is shown in Table 28.

If, by the year 2000, 1 million barrels per day of coal and shale liquids were refined using an average of 4,000 cubic feet of hydrogen per barrel, hydrogen use would come to 0.5×10^{15} Btu per year, a major but not radical increase when compared to the projected range of $2.3\text{-}3.4 \times 10^{15}$ Btu per year for conventional uses. (A comparable amount might be used for coal liquefaction to produce the liquids for refining.) Further growth in the refining of coal and shale liquids could increase the hydrogen demand by an order of magnitude.

PRODUCTION PROCESSES

Steam Reforming

At present, hydrogen is generally manufactured by "steam reforming," a process in which natural gas and steam are reacted at high temperature to produce a mixture of carbon dioxide, carbon monoxide, and hydrogen. (In petroleum refining, most of the hydrogen is produced as a by-product from the catalytic dehydrogenation of naphtha in producing high-octane gasoline, but any major increase in hydrogen demand for refining will require an increase in the use of manufactured hydrogen.) Steam reforming has been gradually improved during its many years of commercial use. The process is carried out by reacting a light hydrocarbon feedstock

	Year		
	1973	1985	2000
Petroleum refining	0.34	0.51	0.5-1.6[b]
Ammonia production	0.34	0.54	0.92
Methanol and other chemicals	0.12	0.22	0.61
Other uses	0.04	0.10	0.25

[a]Based on 322 Btu gross heating value per standard cubic foot.

[b]Quantity will depend on whether residuum cracking is done by coking or hydrocracking.

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \quad (1)$$

Energy for the reaction is produced by burning some of the hydrocarbon feedstock separately in a furnace. The reaction products of the feedstock-steam mixture are then cooled and reacted with additional steam in the presence of a metallic iron catalyst at about 660 F, resulting in the following reaction:

$$CO + H_2O \longrightarrow CO_2 + H_2 \quad (2)$$

The net reaction becomes

$$CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2 \quad (3)$$

with half the hydrogen product coming from the methane feedstock and half from the steam.

Hydrogen can be produced from any light hydrocarbon feedstock that either exists in a gaseous state at the reaction temperature or can be vaporized. Methane is the most desirable feedstock because it has the highest H/C ratio of all the hydrocarbons.

Partial Oxidation

oxygen in a gasification (partial oxidation) reactor at about 2400°F, the following reactions take place:

$$CH_{1.8} + H_2O \longrightarrow CO + 1.9\ H_2 \quad (4)$$

$$CH_{1.8} + 1.45\ O_2 \longrightarrow CO_2 + 0.9\ H_2O \quad (5)$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \quad (6)$$

The heat for the endothermic reaction of equation (4) is supplied by the oxidation reaction of equation (5). Pure oxygen is used instead of air for reaction (5) to avoid diluting the synthesis gas with nitrogen. When the products from the gasification reactor are cooled to about 700°F, any remaining CO is shifted to H_2 by reaction (6). The net reaction for partial oxidation of residual oil thus becomes

$$CH_{1.8} + 0.98\ H_2O + 0.51\ O_2 \longrightarrow CO_2 + 1.88\ H_2 \quad (7)$$

Hydrogen from Coal

Although hydrogen can be produced from coal by a partial oxidation process similar to the partial oxidation of residuum , the process is more difficult to carry out, coal being harder to handle and relatively unreactive. The use of coal adds an additional problem in the need to remove the ash from the gasification reactor. The net result is substantially higher operating costs.

Another problem with coal is its low H/C ratio of about 0.8. With coal as a feedstock, as with residua, hydrogen is produced by reforming, oxidation, and shift reactions:

$$CH_{0.8} + H_2O \longrightarrow CO + 1.4\ H_2 \quad (8)$$

$$CH_{0.8} + 1.2\ O_2 \longrightarrow CO_2 + 0.4\ H_2O \quad (9)$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \quad (10)$$

The net reaction is

$$CH_{0.8} + 0.70\ O_2 + 0.60\ H_2O \longrightarrow CO_2 + H_2 \quad (11)$$

With coal as a feedstock, the gasification reactor is usually run at about 2700°F, the heat required for gasification reaction (8) being supplied by burning part of the coal with oxygen, as in reaction (9). When coal is gasified at a lower temperature, the product is substitute natural gas.

state-of-the-art electrolysis plants require a very high capital invest
ment, but significant progress is being made in reducing capital costs
raising pressures and improving electrodes and electrolytes. (In the
discussion of costs below, the cost of hydrogen production by electro-
lysis is based on a performance similar to that projected for the Gener
Electric Solid Electrolyte Process.)

Presently under investigation in various parts of the world are a
number of processes that produce hydrogen from water by a series of hea
driven multiple-step reactions. While these exploratory studies are in
too early a stage to make accurate estimates of system efficiency and
costs, it appears unlikely at this time that they will be competitive w
the current method of releasing hydrogen from water by combining the
oxygen in the water with the carbon in coal. Processes using nuclear-
generated heat to break water down into hydrogen and oxygen in a closed
cycle must compete with processes in which nuclear-generated heat is us
to produce electricity that is then used to remove the hydrogen from wa
by electrolysis.

The best of the thermochemical processes, offering efficiencies in
the 40-50 percent range, appear to be at least as efficient as electrol
sis with a Rankine-cycle generator working over the same temperature
range, and may be somewhat more efficient.

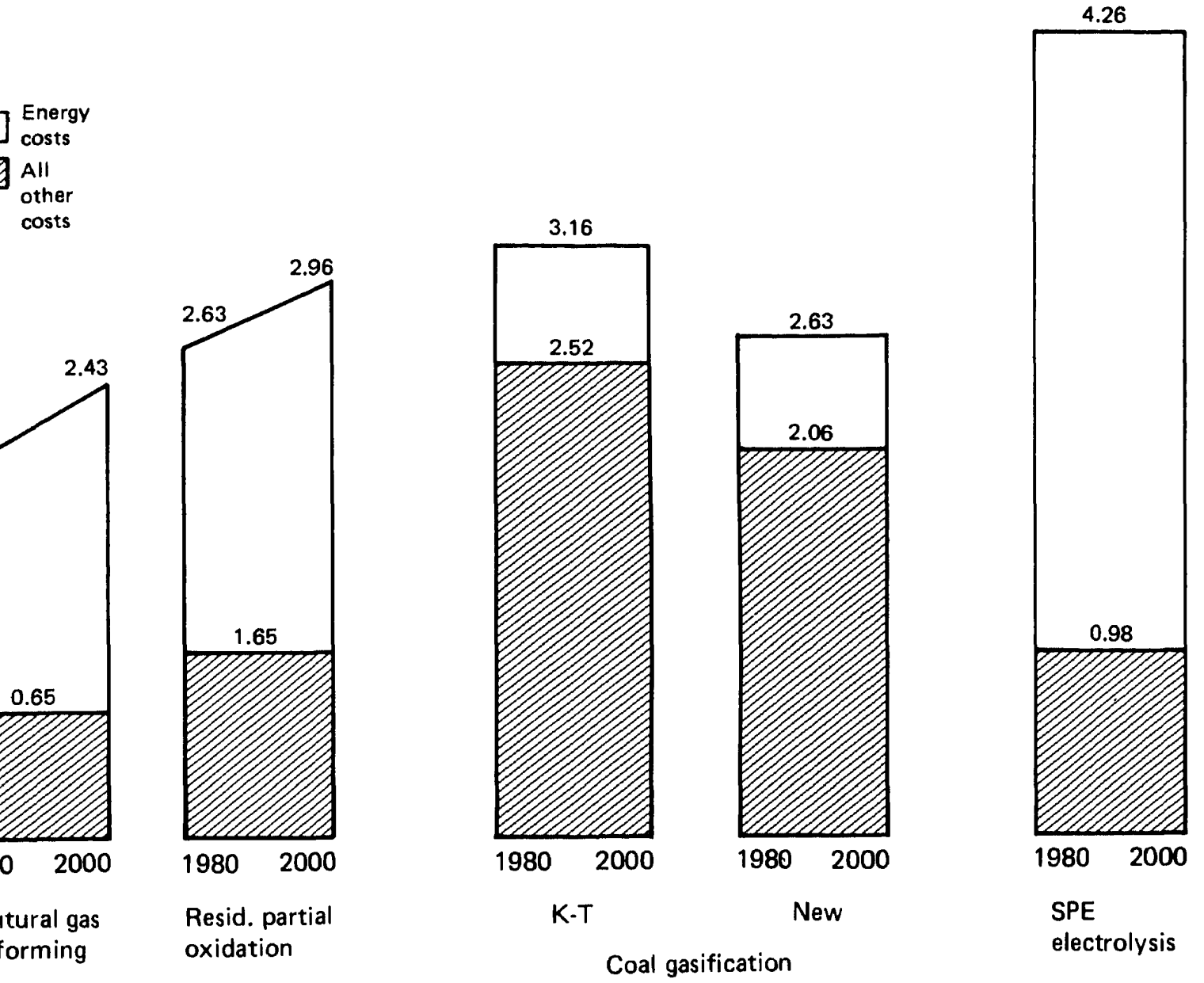
A number of other ways of producing hydrogen are of interest. One
involves the use of iron to decompose water. The hydrogen in the water
is released by the formation of iron oxide, which is then converted
back into iron in a reduction process using gas produced from coal.
A version of this process, under development at the Institute of Gas
Technology with support from a number of utility and industrial groups
and the U.S. Department of Energy, was carried to the pilot plant stage
on a scale that used two tons of coal per day.

The use of CO_2 and H_2S acceptors such as limestone during the gasi
fication of coal can yield refining grade hydrogen in one step, but the
problems, involving limestone life and regeneration, are still serious.

The use of air instead of oxygen in multiple-bed fluid solids syst
has considerable potential if the problems can be overcome. Advances i
technology and design could make this approach attractive.

Comparative Costs

In comparing the costs of the various processes, we assume that the new
generation of closed-cycle thermochemical processes will have costs and
efficiencies comparable to those of new electrolysis processes. Figure



ures on bars are 1980$/1000SCF
0 SCF = 0.322 x 10^6 Btu (gross heat of combustion)

igure 36 Projected costs of hydrogen production by various processes, n plants producing 100 million standard cubic feet per day, at a idcontinent location (Corneil, et al., 1977). Numbers represent 1980 ollars per thousand standard cubic feet (0.322 million Btu gross heat f combustion).

100 million standard cubic feet of hydrogen per day (the quantity required to refine approximately 25,000 barrels of coal and shale liquids). The estimates are based on the work of Corneil et al. (1977). Feedstock and energy costs as given in Table 29 were assumed, along with a before-tax return of 20 percent per year.

As seen in Figure 36:

- Natural gas reforming, with gas at $3.15 per million Btu, provides the lowest cost hydrogen due to the low capital and operating costs.

- Petroleum residuum conversion requires a larger capital investment. Although the feedstock is cheaper than natural gas, the low thermal efficiency combined with the low-hydrogen, high-sulfur content of the residuum results in total feedstock costs that are about the same as the cost of natural gas.

- Partial oxidation of coal (using available Koppers-Totzek technology, for example) requires a very high investment that more than makes up for the lower feedstock costs. The figures shown for the "new" technology are for the same type of process run at a higher pressure (400-500 psi), resulting in high coal conversion and the formation of little methane. (Such a process is currently under development in a program in which Koppers and Shell are taking part.) The "new" technology lowers the costs of the Koppers-Totzek process by about 15 percent, making it competitive with residuum oxidation.

- The projected solid polymer electrolyte (SPE) process will involve a relatively low capital investment for the electrolysis equipment, but electric power costs will be high, depending largely on the capital costs of the generating equipment. The hydrogen produced by this process will very likely cost substantially more than hydrogen produced by the alternative processes. The use of lower cost off-peak electricity will not help to any extent, the saving in power costs being balanced out by the cost of storing the hydrogen.

Although the lowest cost process for hydrogen production at present is steam reforming of methane, a 50 percent increase in the cost of methane would raise the cost of hydrogen to that estimated using the "new" coal gasification technology. The trends now being seen in the discovery and production of methane from the conventional drilling of permeable formations point to short supplies and increasing costs over the years ahead.

stock	1980 dollars per million Btu
ral gas	$3.15
oleum residuum	$2.60 (at $15 per barrel)
	$0.96 (at $21.80 per ton)
tricity	$8.80 (at 3¢ per kWh)

rves will prolong the economic life of hydrogen production from ane, it seems prudent at this time to assume that the production of ogen from coal will eventually displace production from methane.

The cost of producing hydrogen from coal is now nearly competitive the cost of producing it by residuum conversion, and the projected dwide shortage of petroleum after 1990 provides a powerful incentive using coal. During the next century, shortages of coal and concern t the buildup of carbon dioxide in the atmosphere may bring about ansition to hydrogen production by the electrochemical or thermo- ical splitting of water, however.

The capital costs for plants that produce hydrogen from coal are n in Table 30.

The bulk of the cost is in the synthesis gas production,but the cost hift conversion and methanation and the cost of carbon dioxide remov- re sufficiently high to warrant efforts toward cutting these costs .

The capital costs for synthesis gas production shown in Table 30 can roken down as shown in Table 31. There are no easy targets here for jor reduction in costs, although the optimization of the pressure ls can result in a substantial gain.

CONCLUSIONS AND RECOMMENDATIONS

coal, with a capacity of 100 million standard cubic feet per day

Process	Millions of 1980 dollars	
	Koppers-Totzek plant	"New" technology plant
Synthesis gas production (including O_2 plant)	106.4 (72.5%)	82.1 (67.1%)
Shift conversion and methanation	16.7 (11.4%)	16.7 (13.6%)
CO_2 removal	23.6 (16.1%)	23.6 (19.3%)
Total	146.7 (100.0%)	122.4 (100.0%)

Table 31 Breakdown of capital investment costs for synthesis gas production

Process	Percent
Coal preparation and storage	10
O_2 plant and H_2 compression	70
Gasification	20

total cost. The search for ways of reducing this cost should be given a high priority in the synthetic fuels programs of the Department of Energy and of private industry.

- The most appropriate and economical sources of hydrogen for this

limitations and/or environmental considerations may lead to the need for alternatives.

- The cost of hydrogen might be reduced by 10 to 15 percent by optimizing and further developing existing partial oxidation processes for converting coal to hydrogen. An additional 15 percent cost reduction may be obtainable by fully optimizing and developing processes that are now less well developed (e.g., air oxidation in a multiple fluid bed system, the use of CO_2 acceptors such as CaO, or the use of oxygen acceptors like iron).

- The U.S. Department of Energy should give a high priority to the identification and support of R&D and systems approaches to lower cost processes for converting coal and char to hydrogen.

BIBLIOGRAPHY

Cart, E. N., Jr., A. R. Cunningham, and D. Carter. 1978. Alternative Energy Sources for Non-Highway Transportation. Linden, N. J.: Exxon Research and Engineering Company, Government Research Laboratories. (Draft prepared under Department of Energy Contract EC-77-C-05-5408.)

Cornell, H. G., F. U. Hungelmann, and E. W. S. Nicholson. 1977. Production Economics for Hydrogen, Ammonia, and Methanol During the 1980-2000 Period. New York: Exxon Research and Engineering Company (BNL 50663)

Salzano, F. V. 1978. Report presented to Hydrogen Panel, Committee on Advanced Energy Storage Systems, Energy Engineering Board, Assembly of Engineering, National Research Council. Upton, N.Y.: Brookhaven National Laboratory.

8 ENVIRONMENTAL EFFECTS

Substituting coal and shale liquids for the prevailing feedstocks of petroleum refineries will require a careful examination of all of the environmental effects to be encountered. While modern petroleum refineries are generally in compliance with the regulations covering air and water pollution and solid waste disposal,[a] substituting synthetic crudes for petroleum feedstocks can have adverse effects.[b]

The potential adverse effects of substituting synthetic crudes for petroleum depend on the location of the refining operation, the refining scheme required, the methods for handling the products, and the effects encountered in combustion or other end use. A key factor, of course, is the chemical composition of the synthetic crude as compared with that of petroleum. Although pilot-scale tests on shale liquids indicate it is possible and practical (using petroleum refining techniques) to keep the gaseous, liquid, and solid wastes within the limits established by current environmental regulations, the refining of coal liquids is not so far advanced. Problems that have resulted in the past from new economic and technological developments underline the need for better assessments of the environmental, economic, social, and institutional impacts of such developments.

---

[a]Pollution control and the impacts of the standard crude petroleum producing and consuming industries have been reported extensively in the literature. Various studies have dealt with the occupational exposure of refinery workers, the health effects of refinery products on handlers and users, and the effects of emissions and effluents from refineries, blending stations, and service stations on the general population (Bair 1967). Work on fugitive emissions is now in progress.

[b]The site-specific environmental effects associated with the production of synthetic crudes are not considered in this chapter, because these

Although considerable research has been carried out in an attempt to establish acceptable environmental standards, there is still a great need for additional data that can be used to establish conservative, yet practical, parameters for environmental quality. Research is needed to identify and evaluate the risks of exposure to hazardous substances, estimate the costs of reducing the risks, and place the costs and risks in proper perspective. It is well established that the presence of a hazardous substance does not necessarily mean that it will be harmful. There are elements that are essential to life at one concentration and hazardous to life at other concentrations. A substance may be harmless as it exists in nature (or under similar circumstances) but harmful under other circumstances.

The impact of a substance on human health and the environment is a function of the mode of occurrence, concentration, and time. For this nation to become self-sufficient in energy, it is imperative that we know as much as possible about the distribution of the toxic materials that result from our technology and the impacts of these materials on health and the environment. The state of the art is such that identifying and measuring some elements and compounds are often possible at levels well below those that may be harmful.

LOCATION OF THE REFINING OPERATION

The most likely source of shale oil in the relatively near term is the Green River formation at the junction of Colorado, Wyoming, and Utah. The most likely sources of coal oil are the western, midwestern, and Appalachian reserves, with the western reserves now being given the greatest attention.

The production of shale liquids will require extensive mining and extraction operations in areas that have thus far been unaffected by industrial activities. Some of the same problems will be encountered with coal liquids produced from western coals. Even if their viscosities are low enough to permit pumping at ambient temperatures, their chemical instability and immiscibility with heavy petroleum fractions or crude may make it desirable to refine coal liquids at their sources. Thus, in both cases refining will have an additional environmental impact at the source of the raw materials.

CHEMICAL COMPOSITION OF SYNTHETIC CRUDES

The chemical constituents of coal and shale liquids of most importance in determining the refining schemes to be used are the concentrations of heteroatoms (oxygen, sulfur, and nitrogen), polycyclic organic

	Shale Liquids[a]		Coal Liquids[b]		Petroleum[c]	
	Range	Average	Range	Average	Range	Average
Main constituents, wt %						
Carbon	83.1-85.9	84.5	83.0-89.0	86.0	--	86.5
Hydrogen	11.1-12.0	11.5	5.7-11.6	8.6	--	12.3
Heteroatoms, wt %						
Oxygen	0.9-1.89	1.4	0.38-7.15	3.8	--	0.5[d]
Sulfur	0.5-0.9	0.7	0.35-0.57	0.5	0.1-5.3	1.0
Nitrogen	1.3-2.18	1.7	0.77-1.71	1.2	0.02-0.9	0.2
Trace metals, ppmw						
Nickel	1.6-20	--	1-59	--	0.2-124	14.0[d]
Vanadium	0.4-20	--	0.2-275	--	0.1-220	25.4[d]
Iron	40-142	--	6-375	--	--	--
Copper	0.15-11	--	--	--	--	--
Arsenic	10-52	--	--	--	--	--
Titanium	--	--	1-150	--	--	--

[a]See Table 20, Chapter 5.

[b]See Table 25, Chapter 6.

[c]Derived from Fryback (1980), except where noted.

[d]Petroleum Publishing (1973).

liquids, coal liquids, and (for comparison) petroleum crudes, along with their concentrations of some trace metals.

Heteroatoms

Because of their higher heteroatom contents and lower hydrogen contents shale and coal liquids will in general require more hydrogenation than petroleum crudes, but subsequent processing will very likely be similar to the conventional processing of petroleum crudes.

Since the oxygen contents of coal and shale liquids are about 3 to 8 times those of petroleum crudes on the average (Table 32), correspondingly more condensate water with high concentrations of polycyclic organic matter will be produced during the hydrogenation of coal- and shale-derived crudes. However, petroleum refining generates considerably larger amounts of wastewater (from desalting and conversion processes) that contains similar compounds.

The nitrogen contents of coal and shale liquids, 4 to 9 times those of petroleum crudes on the average (Table 32), will result in the generation of significantly more ammonia during hydrogenation. This nitrogen must be removed from the product stream because it would otherwise poison downstream catalysts and degrade the products.

The sulfur in coal and shale liquids must also be removed during hydrogenation to protect downstream catalysts and meet product quality specifications. The sulfur contents of coal and shale liquids are lower than those of petroleum crudes on the average[a] (Table 32), and lower quantities of hydrogen sulfide will be produced. Where the balance between nitrogen and sulfur is conducive to the production of the fertilizer ammonium sulfate, as is frequently the case in the refining of petroleum crudes, it may be possible to use this production to minimize the discharge of sulfur and nitrogen to the environment.

Polycyclic Organic Materials (POMs)

The higher oxygen and polycyclic organic matter contents of synthetic crudes, as compared with petroleum, create the potential for greater concentrations of organic matter in the process wastewater. However, little quantitative information is available. The wastewater results from the separation by condensation of the water generated from the product stream during processing. Since the condensates are saturated solutions under the prevailing process conditions, and since polycyclic materials are more water soluble than paraffinic materials, the condensate waters from the processing of synthetic crudes will have higher concentrations of organic matter than the condensate water from petroleum crudes.

The presence of polycyclic organic materials and hazardous volatile elements in fuel oils will necessitate careful combustion control because of the combustion sensitivity of POMs; incomplete combustion will release particulates, hazardous POMs, and adsorbed toxic elements. POMs can also be created during some complete combustion processes. The use of such fuel oils will need to be carefully monitored if environmental problems

percent shale oil (Southern California Edison, 1976).

The relatively high POM contents of synthetic crudes increase the potential for pollution not only from the hydrogenation step but also from subsequent refining steps. Since the impact will be refinery-specific, it is difficult to predict magnitudes at this stage, but it is certain that the higher POM contents of synthetic crudes will increase the likelihood of carcinogenic, mutagenic, and teratogenic substances in the waste products.

The most noxious POMs of synthetic crudes (i.e., phenols, cresols, and carbolic acids) can readily be degraded biologically. From the limited data available, it appears that biological treatment plus effluent polishing will effectively remove the most important pollutants. Although effluents that are treated biologically show no acute toxic effects on fish, they frequently contain significant concentrations of organic matter that cannot be biologically degraded any further. Little is known of the impact of these substances on the environment.

Trace Elements

Serious environmental problems may also be created by the trace elements in coal and shale liquids; the effects depend largely on the distribution of these elements during processing. The concentrations in the product, by-product, and water phases; on the catalysts; and in the emissions to the environment could range from levels that are not harmful to levels that can affect refinery personnel, users, and the general public. The concentrations in the water phase could create the need for additional wastewater treatment and increase wastewater treatment sludge disposal problems. The concentrations on catalysts could limit the use of thermal regeneration, increasing catalyst requirements by 5 to 20 times and creating serious disposal problems. New methods need to be developed for economically recovering the critical metals in spent catalysts without producing environmental problems.

A serious problem may result from the combustion of end-products that contain high concentrations of trace metals. A test with conventional fuel oil in a utility boiler has shown that the quantities of barium, nickel, arsenic, lead, and mercury in the stack gas can range from a moderate to large fraction of the concentration of these elements in the fuel--13, 16, 32, 78, and 100 percent, respectively (Southern California Edison, 1976). The substitution of synthetic fuels for conventional petroleum-based fuels can therefore seriously aggravate the air pollution problem.

The limited data presented in Table 32 would indicate that the

refining of coal and shale liquids is needed to more clearly delineate the nature of the problems that are likely to be met with gaseous, liquid, and solid effluents. More studies like those made by Battelle-Northwest (Fruchter et al., 1977), TRW, and Denver Research (U.S. Environmental Protection Agency, 1977c) would be useful and could be carried out in conjunction with process R&D. The toxic, mutagenic, teratogenic, and carcinogenic nature of the final products and the possible effects of these products on the general public will also need to be examined in more detail.

REGULATIONS AND CONSTRAINTS

Federal, state, and local governments are now concerned with more than the protection of the health of the general public. In addition to the regulation of the workplace and the quality of the air and water affecting human beings, existing laws and policies protect fish and wildlife life, endangered biological species, scenic rivers, and historical and cultural sites. Public participation is now encouraged in matters affecting the environment.

The most important federal laws on the control of the environment are the following:

- National Environmental Policy Act of 1969 (PL 91-190)
- Clean Air Act Amendments of 1977 (PL 95-95)
- Clean Water Act of 1977 (PL 95-217)
- Safe Drinking Water Act of 1974 (PL 93-523)
- Resource Conservation and Recovery Act of 1976 (PL 94-580)
- Toxic Substances Control Act of 1976 (PL 94-469).

Under the National Environmental Policy Act, the responsible official must file with the Environmental Protection Agency a detailed environmental impact statement for any proposed major federal action significantly affecting the environment. The statement must include descriptions of alternatives to the proposed action, the effects on the "maintenance and enhancement of long-term productivity," and "irreversible and irretrievable commitment of resources" that would be involved.

The Clean Air Act regulates the emission of particulates, sulfur oxides, nitrogen oxides, carbon monoxide, oxidants, lead, and hazardous

Ambient Air Quality Standards (NAAQS). Regional areas that have an air quality better than the NAAQS are designated Prevention of Significant Deterioration (PSD) areas and are allowed incremental increases in emissions for new developments depending on the type of area (e.g., national parks and the like). Areas that do not meet NAAQS are required to obtain offsets in emissions from some other source to accommodate development.

Under the Clean Water Act, various requirements must be met for a permit to discharge wastes into bodies of water. While no specific effluent standards have been set for such discharges from coal liquefaction and oil shale retorting facilities, the refining of synthetic crudes would be subject to the same standards as petroleum refining. For dredge-and-fill operations in a navigable stream, a Section 404 permit must be obtained from the Army Corps of Engineers, with the concurrence of the Environmental Protection Agency. Exceptions to the act may be required for wastewater discharges in western energy-development areas where natural waters, without the discharge of wastes, do not meet water quality criteria. Effluent limitations imposed on the petroleum industry on July 1, 1977, were based on the use of the best practicable control technology currently available. Limitations on water pollution by the industry were also affected by the Settlement Agreement between the National Resources Defense Council and EPA (June 7, 1976) and a U.S. Court of Appeals ruling (August 11, 1976). The settlement agreement now covers a list of 129 priority pollutants that must be taken into account in defining the permissible control technology. Effluent limits have been set on cadmium, copper, cyanides, lead, mercury, zinc, arsenic, nickel, silver, selenium, phenol, and chromium.

The Safe Drinking Water Act regulates the injection and reinjection of fluids into the ground, specifying monitoring and mitigation measures to protect groundwater systems. Permits must be obtained for the reinjection of fluids into the ground in Colorado.

The Resource Conservation and Recovery Act regulates the transportation, storage, and disposal of solids, semisolids, liquids, and contained gaseous wastes from the point of generation to the point of disposal. Under this Act, wastes with certain levels of reactivity, corrosivity, ignitability, toxicity, radioactivity, teratogenicity, mutagenicity, infectiousness, and phytotoxicity are to be classified and listed as hazardous, requiring special transportation to and disposal at waste sites that have EPA or state permits. Waste lubricating oil is already on a special chemicals list and is classified as hazardous. A list of processes generating hazardous wastes includes kerosene filter cakes, lube oil filtration clays, slop oil emulsion solids, and API separator sludge.

The Toxic Substances Control Act deals with recordkeeping, reporting, production conditions, the handling of toxic substances, and the

ency 90 days prior to its manufacture, providing the agency with formation on its use, the quantities to be produced, by-products, sposal practices, and any available data related to health and envi- nmental effects. In addition, the Act stipulates that the manufacturer any new chemical substance may also be required to carry out epidemi- ogical, carcinogenic, mutagenic, and environmental tests. Environmen- l Protection Agency regulation of the use of a chemical may take one three forms: (a) manufacture with no restrictions, (b) manufacture th conditions placed on the handling and use of the chemical, or (c) outright ban.

CONTROL TECHNOLOGIES

Current policy places emphasis on "best practicable," "best avail- le," and "best conventional" control technology, with one exception: itable control technology must be developed where environmental pro- ction criteria are more stringent than current technology can accommo- te.

There are two basic levels of technology for environmental pro- ction:

- The simplest and narrowest approach is effluent or emission treatment, as required by current policy.

- A more comprehensive approach is pollution abatement, an approach to optimum pollution control by means of a techno- logical and economic evaluation of the entire pollution generation system as well as the effluent/emission treatment system.

Government and industry both regard pollution control as the control three separate and independent types of wastes: those discharged to e air, those discharged as liquids, and those discharged as solids. though they may appear as separate and independent types of wastes to me, they are interrelated. There is consequently a need to integrate e treatment of these three types of wastes at their source. An evalu- ion of the entire system in terms of pollution generation, control, eatment, and disposal will provide the most feasible and cost-effective ans of protecting the quality of the environment. The need for techno- gical effectiveness and economy in the national energy program should ovide the motivation for the development of a multipollutant (air, ter, solid waste) release management system.

Although a comprehensive mass balance study of the distribution of llutants among stack gas, wastewater, and solid wastes will be obtain-

The general public has voiced its concern in recent years about industrial pollutants and the effects they may have on the environment and the various forms of life on this planet. Considerable controversy and confusion has resulted from the inability, so far, to accurately assess the risks posed by the emissions and effluents from industrial activity.

One must assume that each of the regulations now in effect is well intended, but each has a cost that should be justified by hard evidence, not supposition. Without generally accepted assessments of the risks and benefits that are likely to result from technological developments, the regulations that ensue will tend to engender public cynicism and slow technological and economic progress.

What is a "safe" level of pollution? Most of the regulations that call for the absence of "traces" of one or another material from air or drinking water were written in an earlier day when the limits of analysis were in the order of parts per million. Current techniques frequently permit the identification of concentrations of parts per trillion, a level at which adverse physiological effects for most, but not all, pollutants are extremely unlikely. Some chemicals have been called into question only because modern ultrasensitive analytical techniques have shown them to be ubiquitous.

In siting new facilities of any kind anywhere, three basic questions need to be answered if potential conflicts among local, regional, and national interests are to be avoided or, at least, resolved. The first question is whether the need for such a facility outweighs its undesirable impacts. If the answer is yes, the next question is whether or not the proposed site is the logical site, or the best site, for such a facility. If the need and the site are accepted, the final question is what must be done to protect the interests of the people that will be affected.

There is, consequently, a need for research on impacts, risks, and other costs, aimed at helping decision makers and the public establish acceptable safeguards and evaluate trade-offs and alternatives. Obviously, means of quantifying such costs at specific sites (especially those that have in the past been little touched by industrial development) are important and should be developed. No matter how precisely we can quantify a risk, an impact, or a benefit, however, it will never be possible to reduce cost/benefit analysis to a matter of mathematical certainty; social values and political interaction will always play the decisive role in determining what is acceptable. Research in the social sciences will help establish decision-making procedures by which the many disparate costs and benefits of development may be weighed in a more orderly fashion.

The committee recommends that efforts be made to do the following:

- Develop principles, criteria, and methodologies for identifying environmental impacts; coordinating the control of gaseous, liquid, and solid wastes; evaluating alternatives and trade-offs, and resolving conflicts among regional and national interests.

- Determine the mass balance and distribution of hazardous substances among the products and wastes of synfuel refineries in order to evaluate potential environmental and health effects.

- Better establish the toxicity, mutagenicity, teratogenicity, and carcinogenicity of liquid, gaseous, particulate, and solid effluents from the refining of coal and shale liquids and the use of the end products, and determine the fates of the hazardous constituents of these wastes in the food chain.

- Develop more cost-effective technology for the treatment of refinery wastewater.

- Develop environmentally acceptable methods for the removal and disposal of the arsenic in shale liquids.

- Develop acceptable processes for regenerating spent catalysts and the recovering of metals from them for reuse.

BIBLIOGRAPHY

Baird, V. C. 1967. Effects of Atmospheric Contamination on Cancer Mortality in Petroleum Refinery Employees. Journal of Occupational Medicine 9(8):415-420.

Beychok, M. R. 1967. Aqueous Wastes from Petroleum and Petrochemical Plants. New York: John Wiley & Sons.

Cameron Engineers, Inc. 1978a. Exxon Reports on Aviation Fuels Production from Shale Oil. Synthetic Fuels 15(2):2-22 to 2-25. Denver, Colo.: Cameron Engineers.

_____. 1978b. Chevron Reports Test Results and Costs of Refining Shale Oil. Synthetic Fuels 15(3):2-1 to 2-10. Denver, Colo.: Cameron Engineers.

_____. 1978c. Sohio Reports Results of Pilot Refining Studies of Paraho Shale Oil. Synthetic Fuels 15(4)(December):2-21 to 2-23. Denver, Colo.: Cameron Engineers.

Colo.: Cameron Engineers.

Center for Strategic and International Studies, Georgetown University. 1978. Where We Agree: Report of the National Coal Policy Project. Boulder, Colo.: Westview Press.

Crawford, K. W., C. H. Prien, L. B. Baboolal, C. C. Shih, A. A. Lee. 1977. A Preliminary Assessment of the Environmental Impacts from Oil Shale Developments. Washington, D.C.: U.S. Environmental Protection Agency (EPA/600/7-77-069).

Ewing, R. C. 1973. Amoco Installs Fluid-Bed Incinerator. Oil and Gas Journal 71(4):103-106.

Fryback, M. G. 1980. Personal Communication.

Fruchter, J. S., M. R. Petersen, J. C. Laul, and P. W. Ryan. 1977. High Precision Trace Element and Organic Constituent Analysis of Oil Shale and Solvent-Refined Coal Materials. Richland, Wash.: Battelle Pacific Northwest Laboratories (BNWL-SA-6001).

Ghassemi, M., D. Strehier, K. Crawford, and S. Quinlivan. 1978. Applicability of Petroleum Refinery Control Technologies to Coal Conversion. Washington, D.C.: U.S. Environmental Protection Agency (EPA/600/7-78-190).

Gold, H., and D. J. Goldstein. 1978. Water-Related Environmental Effects in Fuel Conversion. 2 vols. Washington, D.C.: U.S. Environmental Protection Agency (EPA/600/7-78-197A,B).

Gold, H., J. A. Nardella, and C. A. Vogel. 1979. Fuel Conversion and Its Environmental Effects. Chemical Engineering Progress 75(8):58-64.

Halper, M. 1974. Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Petroleum Refining Point Source Category. Washington, D.C.: U.S. Environmental Protection Agency (EPA/440/1-74-014-A).

Jahnig, C. E. 1975. Evaluation of Pollution Control in Fossil Fuel Conversion Processes. Gasification: Section 8. Winkler Process. Washington, D.C.: U.S. Environmental Protection Agency (EPA/650/2-74-009-J).

Jewitt, C. H., and G. D. Wilson. 1978. Comparative Characterization and Hydrotreating of Coal, Shale, and Petroleum Liquids. Advances in Chemistry Series 78(170):243-254.

National Research Council. 1977. Assessment of Technology for the Liquefaction of Coal. Committee on Processing and Utilization of Fossil Fuels, Commission on Sociotechnical Systems. Washington, D.C.: National Academy of Sciences.

Petroleum Publishing Company. 1973. Evaluation of World's Important Crudes. Tulsa, Okla.

Singer, P. C., F. K. Pfaender, J. Chinchilli, A. F. Maciorowski, and J. C. Lamp III. 1978. Assessment of Coal Conversion Wastewaters. Washington, D.C.: U.S. Environmental Protection Agency (EPA/600/7-78-181).

Southern California Edison. 1976. Emission Characteristics of Paraho Shale Oil as Tested in a Utility Boiler. Los Angeles: Southern California Edison/Paraho Oil Shale Demonstration, Inc.

Tencer, B. 1978. Coastal Zone Management--The Role of Interstate Commissions on Energy Siting Issues; On-Shore Impacts of OCS Activity. Paper presented at Environmental Regulation Conference, Region III, Philadelphia, Pa., May 18-19.

Thoem, T. L. 1979. EPA Oil Shale Research-Regulatory Program. Twelfth Annual Oil Shale Symposium Proceedings, ed. James H. Gary, pp. 43-51. Golden, Colo.: Colorado School of Mines.

U.S. Environmental Protection Agency. 1973. Development Document for Effluent Limitations Guidelines and Standards of Performance, Petroleum Refining Industry. Washington, D.C.: U.S. Environmental Protection Agency (EPA/440-1-73-014-B).

_____. 1974. Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology. Washington, D.C.: U.S. Environmental Protection Agency (EPA/650/2-74-118).

_____. 1977a. Advanced Fossil Fuels and the Environment: An Executive Report. Washington, D.C.: U.S. Environmental Protection Agency (EPA/600/9-77-013).

_____. 1977b. Energy/Environment II (Decision Series). Washington, D.C.: U.S. Environmental Protection Agency (EPA/600/9-77-012).

_____. 1977c. Trace Elements Associated with Oil Shale and its Processing. Washington, D.C.: U.S. Environmental Protection Agency (EPA/908/4-78-003).

_____. 1979. Effluent Limitations Guidelines (BATEA), New Source Performance Standards, and Pretreatment Standards for the Petroleum

SSR, and in Water Organisms. Environmental Health Perspectives 30: (June):211-216.

Weston, R. F. 1950. Separation of Oil Refinery Wastewaters. Industrial and Engineering Chemistry 42(April):607-612.

_____. 1953. The Waste Disposal Problems of the Petroleum Industry. In Industrial Wastes: Their Disposal and Treatment, ed. Wilhelm Rudolphs. American Chemical Society Monograph No. 118, pp. 419-449. Washington, D.C.: American Chemical Society.

_____. 1971. Water Pollution Control Implementation Administrative Problems. Water and Sewage Works 118(11):77a-83a.

_____. 1976. When is Waste Hazardous? When Does It Become a Problem? Proceedings of Hazardous Waste Management Seminars, ed. Esther H. Montgomery, Vol. 1, pp. 1-80. Philadelphia, Pa.: Pennsylvania Environmental Council.

Weston, R. F., and R. A. Baker. 1956. Biological Treatment of Petroleum Wastes. Sewage and Industrial Wastes 28(1):58-69.

Weston, R. F., and W. B. Hart. 1941. The Water Pollution Abatement Problems of the Petroleum Industry. Water Works and Sewerage 88: 208-217.

Weston, R. F., and R. G. Merman. 1954. The Chemical Flocculation of a Refinery Waste. Proceedings. Addresses and Reports Delivered at Meetings of the American Petroleum Institute, Vol. 34, pp. 207-225. New York: American Petroleum Institute.

Weston, R. F., and R. Morrell. 1977. Treatment of Water and Wastewater for Removal of Heavy Metals. Paper presented at Intensive Short Course in Viruses and Trace Contaminants in Water and Wastewater, University of Michigan, Ann Arbor, Mich., January 26-28.

9 HEALTH EFFECTS

For over a hundred years coal tars, heavy petroleum fractions, and shale oil have been known to cause abnormal skin growths and sometimes fatal skin cancer in workers exposed to them. The occupational health risks of refining and handling coal- and shale-derived liquids must therefore be given careful study, along with the risks to consumers who use the refined products. Of greatest importance is the ability of coal tars to cause skin cancers and possibly other cancers, due to relatively high contents of high-boiling-point polynuclear aromatic and heterocyclic compounds. Shale oil and petroleum crudes contain less of these substances, although severe thermal treatment greatly increases their concentrations, so that certain heavy petroleum fuel oils produced by severe cracking are today given special handling in refining and use.

During the development of the petroleum industry over the past century, increasing attention has been paid to the environmental and health effects of their refining and use. Of particular importance have been occupational health problems and pollution of the environment by refinery effluents and combustion of refined products.

The introduction of coal- and shale-derived liquids will tend to increase the potential for health impacts. This chapter discusses the specific hazards, concentrating on the problems posed by carcinogens, cocarcinogens, and mutagens in the liquids and in their refined products. The experience of the petroleum industry, where similar problems have been successfully dealt with, will be reviewed as a model from which we may draw inferences about the safe handling of synthetic liquids.

HEALTH EFFECTS OF PETROLEUM REFINING AND HANDLING

The carcinogenic potential of petroleum crudes is low, varying from crude to crude (Leitch, 1922; Twort and Twort, 1931; Schwartz, 1934; Antonov and Lints, 1960; Emmet, 1975). Differences in the carcinogenicity of 16 different crudes have been reported by Leitch (1922), and Heiger and Woodhouse (1952) have shown the carcinogenicity of petroleum crudes to

examining boiling point fractions and other factors. In experiments reported by King (1969) and the United Kingdom Medical Research Counci (1968), crudes that boiled at temperatures above 650°F (350°C) were found to be the most carcinogenic, but specific carcinogens were not isolated. As a result of these experiments, the carcinogenic potency of a petroleum crude was thought to be due to the interaction of weak carcinogens.

Studies to date show that the carcinogenic potentials of various coal, oil shale, and petroleum products generally correlate with their boiling points. Animal tests also indicate a general correlation betw carcinogenicity and the presence of certain aromatic compounds, such a benzo(a)pyrene. The question is whether the increase in carcinogenici with temperature is due to the selection and concentration of carcinog that are already present in the crude or to de novo synthesis by pyrol during refining. When Smith et al. (1951) compared the carcinogenicit of certain virgin gas oils, crudes, and high-boiling-point catalytical cracked oils, they found that the virgin feed to the cracking process showed moderate carcinogenic activity while the residuals and the crud from which they were distilled showed none.

Experiments carried out with animals showed that the high-boiling point fractions of catalytically cracked oil had carcinogenic activiti comparable to those of active coal tars. In skin painting tests on mice, rabbits, guinea pigs, and rats, the mice were found to be suscep tible to the development of cutaneous malignancies and the rabbits wer found to be prone only to early papilloma (benign epithelial tumors). The guinea pigs and rats were unresponsive. When different boiling fractions were distilled from catalytically cracked oil, a sharp cut-o in carcinogenicity was noted. The 700-800°F (371-427°C) fractions pro duced only papillomas. Higher boiling-point fractions produced carci- nomas, the effect peaking with the fractions in the 950-975°F (510-524 range.

Dietz et al. (1952) investigated the conditions under which carci genic compounds formed in refining processes and found that the major carcinogenic component of the refinery product was in the 700-985°F (370-550°C) fractions. They also found, by chemical analyses and carcinogenic potency tests with mice, that the materials in the boilin point range associated with carcinogenicity could be reduced to zero by recycle catalytic cracking, and studied the effect of varying the recycle percentages.

Dietz et al. (1952) also investigated the possibility of disposin

ction boiling above 800°F (427°C) and decrease the quantity of non-
matics. Despite the increase in the quantity of aromatics, tumor
ency does not seem to be appreciably higher than that of the clarified
feedstock. Thus, further thermal cracking of catalytically cracked
will reduce its carcinogenic potency.

OCCUPATIONAL STUDIES

e years back, a number of investigators reported on the incidence of
n cancer in certain petroleum refinery workers and the occurrence of
n lesions on machinists using petroleum-derived cutting oils (Davis,
4; Kennaway, 1925; Schwartz, 1934).

Since then, additional studies have shown that the tumor-induction
ency of the low-boiling-point fractions of petroleum may be enhanced
the presence of some substances that are not, by themselves, carcino-
ic. Holt et al. (1951) found that a 1:1 mixture of distillate oils
h boiling points above and below 700°F (370°C) usually produced more
ors than fractions from the same crude with boiling points in the
-810°F (370-500°C) range. They attributed this paradox to the pres-
e of noncarcinogenic long-chain paraffins (C_{10}-C_{16}) and alkyl deriva-
es of cyclohexane, benzene, and naphthalene in the lower boiling
nt fraction.

Subsequently, Horton et al. (1965) attributed the tumorigenic
ivity of cutting oils to the elemental sulfur and organic sulfur com-
nds added, finding that the addition of elemental sulfur, benzyl di-
fide, and tetrabutyl polysulfide shortened the latency period in tumor
eriments.

The toxicity of highly volatile petroleum products affects the work-
in a variety of industries that use these products (e.g., industries
t produce paints, solvents, and cleaning compounds). Even the slight
osure of gasoline handlers has a significant effect. A correlation
ween urinary phenol and exposure to gasoline has been reported in the
erature (Sherwood, 1972), and there is anecdotal evidence that an un-
al exposure to gasoline from industrial accidents can lead to toxic
turbances. The toxic effects of gasoline are believed to be due to
benzene and benzenelike single-ring aromatics and phenols that are
sent in gasoline in low concentrations. Benzene concentrations of
-3.2 ppm have been measured in the air near bulk-loading installations
gasoline with 3.1-5.8 percent by volume benzene. Gasolines with
her benzene concentrations have given atmospheric concentrations of up
9.4 ppm (Parkinson, 1971).

threshold limit of 10 ppm set by the American National Standards Institute for the handling of gasoline with a benzene content of 5 percent or less (American National Standards Institute, 1969, 1975).

Now that benzene is known to be a leukemogenic agent (Eckhardt, 1973), the potential hazards inherent in gasoline-handling and petroleum refinery operations cannot be dismissed. Although a 1974 epidemiological survey of 38,000 refinery workers exposed to low-level benzene concentrations for 10 years did not show the health conditions of these workers to be statistically different from those of the general populations in the countries studied (Thorpe, 1974), this survey suffered from the lack of proper controls, as have many other occupational risk assessments in the past.

The potential risk of leukemia from petroleum products should continue to be examined. A 1975 survey of rubber industry workers indicates that the incidence of lymphatic leukemia in workers exposed to solvents is twice that of unexposed workers (McMichael et al., 1975).

In 1974, the American Petroleum Institute published the results of a survey of causes of death among petroleum refinery workers (Tabershaw/Cooper Associates, 1974, 1975). The study selected workers in 17 of the nation's 251 refineries, to provide a representative sample according to location, ownership, and size. The mortality study involved 20,163 workers with a total of 142,298 years of observation. Every worker included in the study had worked in one of the refineries for at least one year between January 1, 1962 and December 31, 1971. Ninety-nine percent had been successfully traced as of the final report on September 23, 1975.

Sixty-four percent of the group, representing 76 percent of the years of observation, were men hired before 1952; the average length of service was 20 years. There were 1,194 deaths in the group, and death certificates were obtained for 1,185.

The major findings of the study were as follows:

1. The Standardized Mortality Ratio (SMR) for all causes was 69.1, compared to 100 for a comparable U.S. male population.

2. Mortality from CV-renal disease (SMR 74), digestive cancer (SMR 86), and ulcers of the duodenum (SMR 88) was inversely related to estimated exposure to atmospheric hydrocarbons.

3. Mortality from respiratory cancer increased with increased estimated exposure, but remained below the expected value

significant.

ilar study in the United Kingdom (Rushton and Alderson, 1980) has tly published findings that tend to corroborate these results.

SHALE OIL REFINING AND HANDLING

s for the commercial production of fuels, waxes, and chemicals oil shale have been operated during the last 140 years in France, alia, Estonia, Sweden, Spain, Manchuria, the Republic of South a, Germany, and the People's Republic of China. Information on ssociated health effects has come mainly from Scotland, Estonia, he United States.

Scottish Studies

otland, oil shale has been used since the late 19th century for roduction of ammonia, naphtha, lubricating and illuminating oils, olid paraffin (Leitch, 1922). During the early 20th century, ts began to appear of an increased incidence of cancer among ffin and oil workers in the shale oil industry and among workers extile factories (Scott, 1922; White, 1926; Henry, 1937). The lubri- g oils used extensively in the spinning-mules of textile factories to be linked to cases of cutaneous, penile, and scrotal "mule- ner's cancer." Extensive experiments with animals (Twort and Twort,) showed not only that shale oil products were more carcinogenic comparable petroleum products but also that the high-boiling-point tions of shale oil were more potent than the low-temperature frac- s; the carcinogenicity increased in fractions boiling at temperatures 750°F (400°C).

Twort and Twort concluded that "shale oil contains compounds easily ered carcinogenic at relatively low temperatures (as compared to coal), while at higher temperatures additional and more active compounds formed." When medicinal liquid paraffin was autoclaved at 715°F °C) they found that it too gave definite evidence of tumorigenicity.

Twort and Twort were unable to identify the carcinogenic compounds hale oil, but Berenblum and Schoental (1943), using spectrofluorome- reported approximately 1 percent benzo(a)pyrene (BaP) in blue shale but no significant evidence of BaP in unretorted shale. Beren- and Schoental also showed the presence of other carcinogenic com- ds in the shale oil, reporting the tumor potencies of different tion groups.

(930°F, 500°C) process that yields oil containing paraffins, naphtha
lenes, olefins, aromatic compounds, oxygen, phenols, sulfur-containin
compounds, and nitrogen-containing compounds, and (b) a high-temperat
(1830-2200°F, 1000-1200°C) chamber-oven process yielding more aromati
Estonian shale and its derivatives contain a relatively large amount
of phenol-related compounds (Veldre and Janes, 1979).

After an examination of 215 shale oil workers, Kung (1972) repor
symptoms of intoxication (including headaches), sleep disorders, irri
bility, fatigue, and disturbances of the central nervous system (Veld
and Janes, 1979). Urinary excretion of phenols was noted in exposed
workers but it did not appear to be correlated with the length of exp

In a subsequent study of 2,069 workers who had been employed in
Estonian shale oil industry for 10-20 years, Purde and Rahu (1979) fo
that the incidence of skin cancer in the women in the group was signi
cantly higher than it was in the general population, and that the
cancers tended to appear at an earlier age.

Since 1951, animal tests of the carcinogenic potency of Estonian
shale tars, retort oils, and commercial products have been carried ou
by painting them, in either concentrated or diluted form, on the back
of mice (Bogovski and Vinkmann, 1979). In addition to irritation of
the skin and mucous membranes, investigators noted signs of neuromusc
excitability and systematic alterations that indicated the possible a
sorption of toxic components through the skin, symptoms similar to th
reported by Kung (1972). The most carcinogenic fractions were those
retorted at high temperatures; blends containing as little as 10 perc
of the most carcinogenic material (chamber-oven oil) were found to ha
the same effect as the undiluted oil. Experiments with chromatograph
fractions of aromatic compounds of chamber tar showed no strong corre
tion between tumor potency and BaP content. Studies of the effect of
coking on BaP concentrations and tumorigenicity showed that the distil
from coking had less than 25 percent of the BaP content and essentia
none of the BaP tumor potency of its chamber-oven tar precursor (Bogo
and Vinkmann, 1979).

In animal studies of the carcinogenic and cocarcinogenic action
water-soluble phenols from Estonian oil shale, Bogovski and Mirme (1
detected only weak carcinogenic activity in crude water-soluble phen
recovered from process wastewater. Two-stage experiments they desig
to promote the formation of tumors showed that crude phenols had pos
effects and more refined products had weak or undetectable effects.

Studies have indicated that the general toxicity of Estonian sh
oil is greater in the higher boiling-point materials (Veldre and
Janes, 1979; Blinova et al., 1974). The studies made suggest that t

various phenolic fractions all showed considerable toxicity.

In animal studies using acute exposures, death was associated with us neurological signs. With the longer exposures, there were signs sfunction of the central nervous system, anemia, and leukopenia (a e reduction in the blood's white cell count), and decreases in the ase and perioxidase enzymes, SH groups, and glucose levels in the . There was also evidence of decreased kidney and liver function.

U.S. Studies

few studies of oil shale-related health effects were made in this ry until recently. A 1955 report on skin lesions was inconclusive ingham, 1955), but a report the following year showed that crude oil and several fractions boiling above 1300°F (700°C) were car- enic to the skin of mice, although their potencies were less than of heavy oils from coal hydrogenation (Hueper, 1956a, 1956b). reports on tests with mice showed that crude shale oil and petro- products had approximately one-fifth the carcinogenic potency al tar, and that hydrotreated shale oil was approximately one- enth as potent (Atwood and Coomes, 1974; Coomes, 1976). Another t study shows the following incidence of skin cancer in mice from doses of petroleum, shale, and coal crudes: 53 percent from a ifuged Synthoil coal crude, 40 percent from a shale crude from ified *in situ* pilot plant, 37 percent from a COED coal crude, and cent from a blend of petroleum crudes from California, Alberta, a, Iran, Louisiana, and Arabia (Holland *et al.*, 1979).

Considerable experimental data have been obtained in the past decade short-term tests of mutagenic action (e.g., the Ames test, forward everse mutations with *E. coli* and *Saccharomyces cerevisae*, and the inked recessive test in *Drosophila*). A useful first-order predictor tagenesis, the Ames test is also being considered as a predictor of nogenesis, because of the strong correlation between the mutageni- and carcinogenicity of pure compounds (Ames, *et al.*, 1973; Ames ., 1975). This test has been carried out with various petroleum, , and coal crudes, process water effluents, and so on. A central itory now exists for the collection and distribution of materials iological and chemical testing to cooperating investigators (Coffin, Coffin *et al.*, 1979). Preliminary findings now available from -term testing may be relevant to problems associated with refining. ional data are to be presented at an intergovernmental agency work- sponsored by the Environmental Protection Agency and Oak Ridge nal Laboratory in mid-1980.

A great deal of useful information has also been obtained by combin-

Guerin et al., 1979; Epler et al., 1977). Extractive fractionation (Table 33) has shown that the basic fraction has the strongest mutagenic activity, on a weight/weight basis, although a comparison on the basis of relative concentrations shows that it is the neutral fraction that contributes most to the total activity. Chemical fractionation has shown that the hydrophobic H-bonding fractions (amines, phenols, etc.) and the tetraaromatic fractions have the greatest mutagenic activity. Guerin et al. (1979) and Epler et al. (1979) found, on further examination of the basic fractions, that the mutagenic activity is contained largely in an acetone subfraction from the ether-soluble base fraction containing such compounds as dibenzacridenes and azobenzopyrenes. However, continued studies by Guerin et al. (1979) indicate that the unusual mutagenicity of the basic fraction in raw coal and shale liquids may be due to the presence of polycyclic aromatic primary amines; Pelroy et al. (1979) also demonstrated the presence of amines in this fraction. No significant basic fraction is contained in crude petroleum. These data suggest that the presence of the highly mutagenic compounds such as the primary amines most probably explain the differences in the mutagenicity and carcinogenicity of coal and shale liquids and petroleum. Hydrotreating would remove the mutagenic activity of the basic fraction as well as that of the neutral fraction.

The Tosco Corporation has been looking into the toxicity (particularly the carcinogenicity) of shale oils for a number of years. Animal studies from 1975 to 1978 at the Eppley Institute for Research in Cancer and Allied Diseases (Omaha, Nebraska) and at Bioresearch Consultants (Cambridge, Massachusetts) have shown that petroleum crude oil and shale oil coke have carcinogenic potentials equivalent to, or lower than, those of common petroleum refinery products and intermediates. The studies have effectively demonstrated that the refining of shale oil by hydrotreating significantly reduces its carcinogenicity:

- Animals constantly exposed over their lifetimes to massive concentrations of oil shale and Tosco II spent shale by skin contact, ingestion, and inhalation did not develop cancer or any acute toxicities.

- Intratracheal instillation of oil shale, Tosco II spent shale, Tosco II atmospheric effluent, or shale oil coke in hamsters did not cause lung cancer.

The American Petroleum Institute has conducted a major testing program to determine the biological impact of raw shale, spent shale, and shale liquids from various sources and processes (Table 34). Related studies are being carried out by Colony Development, the U.S. Environmental Protection Agency, and the National Institute of Occupational

		activity[c]
ctive fractionation		
ium hydroxide insolubles	256	3
k acid 1 (WA_I)	185	1
k acid 2 (WA_E)	52	1
ong acid 1 (SA_I)	0	0
ong acid 2 (SA_E)	159	1
ong acid 3 (SA_W)	160	1
sic 1 (B_{Ia})	1,377	3
sic 2 (B_{Ib})	800	2
sic 3 (B_E)	952	68
sic 4 (B_W)	223	1
tral	112	97
Total		178
dex gel romatographic ctionation		
drophilic	1,300	78
ymeric 1	54	3
onding	1,040	52
ymeric 2	0	0
phatic	180	108
/diaromatic	24	3
/tetraaromatic	132	7
traaromatic	1,220	49
Total		300

e derived crude oil "B", separate aliquots about six months apart.

ertants per milligram of fraction using TA98, S-9, and Aroclor 1254
t and Twort, 1931).

ertants per milligram of starting material computed by multiplying
vity of fraction by weight percentage of total recovered weight
ituted by the fraction.

Table 34 API shale toxicity testing program

Material	Process	Subject area					
		Acute toxicity	Carcino-genesis	Chronic inhala-tion	Muta-genesis	Terato-genesis	Analytical
Raw shale							
Anvil Points		X	X	X	X	X	X
Colorado "C-a" tract		X	X				X
White River		X	X				X
Shale oil							
Parachute Creek	Tosco	X	X		X	X	X
Anvil Points	Paraho D[a]	X	X		X	X	X
Anvil Points	Paraho D[b]	X	X				X
Parachute Creek	Union B	X	X		X	X	X
Spent shale							
Parachute Creek	Tosco	X	X				X
Anvil Points	Paraho D[a]	X	X	X	X	X	X
Anvil Points	Union B	X	X				X
Parachute Creek	Union SGR	X	X				X

[a]Direct fired.

[b]

Indirect Liquefaction

Although this report focuses primarily on direct liquefaction, at least passing reference should be made to the liquids produced by indirect liquefaction processes (Fischer-Tropsch, methanol, methanol to gasoline, and methanol to methyl tertiary butyl ether). Free of nitrogen and sulfur contaminants, all these liquids will have acceptable combustion emission levels. Toxic to varying degrees when ingested, inhaled, or absorbed through the skin, none of them is likely to contain "chronic toxins" (i.e., carcinogens).

The more complex mixtures (Fischer-Tropsch oils) have been tested on mice (Hueper, 1956a, 1956b). Cutaneous applications and injections did not result in any observable cancers, but liver degeneration was noted in heavily dosed animals. The absence of carcinogenic activity was undoubtedly related to the aliphatic (as opposed to polynuclear) structure of Fischer-Tropsch liquids.

Direct Liquefaction

The incidence of skin cancers among individuals working with the products of coal pyrolysis and coal combustion has been noted for more than 200 years (Pott, 1775; von Volkmann, 1875; Yamagawa and Ichikawa, 1915; Hueper, 1942). During the early 20th century, attempts were made to understand the problem by inducing malignant growths and tumors in animals with cutaneous applications of coal tar and extracts from coal and soot (Yamagawa and Ichikawa, 1915; Tsuitsui, 1918).

A decade or so later, Kennaway and Hieger (1930) showed that it was possible to produce cancer with a synthesized compound (1,2,5,6 dibenzanthracene) that is a component of coal tar, and Cook et al. (1933) established the carcinogenicity of benzo(a)pyrene. Other investigators subsequently reported on the carcinogenic activities of polynuclear aromatics, dibenzacridines, dibenzcarbazoles, aniline dyes, and many other compounds synthesized from coal, petroleum, and other feedstocks (Shubik and Hartwell, 1957; Gerarde, 1960). Gerarde discusses the toxicity of aromatic hydrocarbons at some length.

Pyrolysis

Various forms of coal pyrolysis were used prior to 1920 to produce illuminating gas, tar, refined tar products, and coke. The health problems of the workers have been reported in a number of U.S., British, and German publications (von Volkmann, 1875; Tillmanns, 1880; Schuchardt, 1885; Legge, 1911, 1922a, 1922b; Kennaway, 1924a, 1924b; Heller, 1930).

tion of coke for blast furnaces (and, at one time, for water gas pr
tion) (Bruusgaard, 1959; Doll et al., 1965; Batteye, 1966; Doll et
1972; Redmond et al., 1972; National Research Council, 1977). Coke
are batch devices in which the emissions during charging and discha
are unavoidable (Lawther et al., 1965; Batteye, 1966; Treibl, 1967;
et al., 1974). The synthetic fuel processes now under study, on th
other hand, are continuous processes in which products are withdraw
under controlled conditions, as in petroleum refineries. There wil
still be risks, however, since the primary liquid products are carc
genic (Forney et al., 1974). Such risks must be minimized by appro
plant design and hygienic operating practices.

Little has been published on the health effects of the trace e
in coal that are carried into the coal liquids during each of the l
faction processes. A start has been made on the concentrations of
elements in crude coal liquids (see Table 25, Chapter 6), but more
definitive data on the fates of these trace elements during the liq
tion and refining processes are needed. A total of 38 elements (in
tion to the basic carbon, hydrogen, and oxygen) have been identifie
in coal (National Research Council, 1977).

Coal Hydrogenation (Solvent Extraction and Catalytic Liquefaction)

As solvent extraction and catalytic liquefaction are alternative fo
of coal hydrogenation, it is reasonable to expect their health effe
to be similar.

In 1956, Hueper reported that eight of the nine fractions from
hydrogenated coal liquid products of the U.S. Bureau of Mines' Berg
pilot plant produced cancers in rats, mice, and rabbits; the carcin
potency increased as the boiling point of the fraction increased. S
activity was still present in unfinished gasoline, but none was fou
finished gasoline.

Since solvent-refined coal (SRC) liquids are highly aromatic a
contain large quantities of material boiling above 600°F (315°C), o
would expect them to be carcinogenic. Cutaneous applications on mi
at the Kettering Laboratories showed that, while the solution of SR
used was weakly carcinogenic, the hydrogenated bottoms and solvent
moderately potent (National Research Council, 1977).

At the close of World War II, eight volumes were written on al
aspects of coal and tar hydrogenation by specialists from I. G. Far
Industrie, Ludwigshafen (Prev, 1945). No detailed health data were
cluded in this extensive summary, but a discussion on condensed aro
showed that the authors were aware of the health hazards:

found were more in the nature of byproducts, in most cases undesired, in many cases even to be considered harmful, and efforts were therefore made to keep their amounts as low as possible.

spite their awareness of the carcinogenicity of high-boiling-point ndensed aromatics, it seems reasonable to assume there were no major alth problems in German industries because of the low boiling points the products handled.

In 1952, a 300-ton-per-day hydrogenation pilot plant, set up by rbide and Carbon Chemicals to produce various chemicals from coal, began affect the skin of a large number of workers (Ketcham and Norton, 1960; wry, 1963). When 2537 Å ultraviolet light was used to study the expo- re of the workers, the examiners noted various patterns of fluorescence, aging from a general fluorescence of the face to streaks and/or smudges fluorescence on various parts of the body. Air samplings showed con- ntrations of BaP that varied from 0 to 1870 mg/m^3. In clinical studies 359 of the male workers with a mean age range of 36-40 years, 51 were and to have a total of 63 skin abnormalities. After an examination of st of these abnormalities, 18 were classified as cancerous and 36 were assified as precancerous; 2 others were suspected of being cancerous the evidence was not clear cut. An analysis of the exposure times d to the conclusion that exposures of nine months or more were increas- g the skin cancer rate significantly, possibly to as much as 16-37 nes the rate for the same age group in the general population.

By means of skin painting tests on mice, various process streams at rbide and Carbon Chemicals were compared with a positive control (methyl olanthrene). The results showed that the tumorigenicity of the streams s proportional to the boiling point, the light oil portion indicating activity (Table 35). Although the tumorigenicity was still substantial en the amount of pasting oil remaining in the mix was as little as 2 rcent, it could be reduced appreciably by washing the skin after expo- re or applying protective cream before. In tests of the effect of lution (with benzene), the latent period was found to increase in pro- rtion to the percentage of benzene.

Carbide and Carbon Chemicals later required that its workers wear otective clothes and that they follow a regimen of showers and changes clothing. However, the plant was closed shortly thereafter; follow- studies are underway but incomplete. The company's safety and health ocedures and their clinical, experimental, and control programs indicate e type and magnitude of effort necessary to cope with the problems countered in coal hydrogenation (Sexton, 1960; Weil and Condra, 1960; tcham and Norton, 1960).

Material	Boiling Point (°C)	Tumor index	Cancer index	Tumor ratio[a]	Cancer ratio[a]
Middle oil stream	260 to 320	46	15	35	31
Light oil stream residue	260 to 380	66	38	46	45
Pasting oil	320 to 450	94	75	80	76

[a]Ratio of mean latent period of methyl colanthrene to the mean latent period of material, multiplied by 100.

Source: Weil and Condra (1960).

HANDLING AND USE OF OIL SHALE AND COAL PRODUCTS

Gasoline

Since it is reasonably certain that gasoline produced from oil shale and coal will be indistinguishable from gasoline produced from petroleum, no new problems are anticipated in handling and using synthetic gasolines.

Mid-Distillates

The problems of handling and using mid-distillates from petroleum (e.g., heating oils, diesel fuels, and kerosene) have been relatively minor, since they contain little or none of the more active polynuclear aromatics. But the situation will be quite different with mid-distillates produced from coal and oil shale. The problem may be more severe with the former, since coal liquids are more highly aromatic and have a carcinogenic activity that is comparable to or greater than that of the more active cracked petroleum fractions. Limited tests indicate hydrotreated shale oils are significantly less potent (Atwood and Coomes, 1974; Coomes, 1976).

Further study is needed of ways of reducing the hazards of handling

Residual Fuels

Since SRC and heavy hydrogenated coal oils are environmentally acceptable as boiler fuels, they will very likely be used for this purpose initially. These liquids are actively carcinogenic, however, and will require special handling by industrial users to avoid prolonged cutaneous contact. If the heavy refined shale oils are also actively carcinogenic, they will require similar precautions. Information on the trace metals in the heavy synthetic liquids has not yet been published.

Combustion Particles

Added to a long-standing concern about the carcinogenicity of soot from the incomplete combustion of coal is a newly discovered concern--the carcinogenicity of the polynuclear hydrocarbons (PNH) that result from the incomplete combustion of organic matter.[a] An active study of this matter is being carried out at the Massachusetts Institute of Technology using new quantitative assay techniques that are similar to the Ames test (Shopek et al., 1978a, 1978b). An extensive program to evaluate the mutagenicity of particles from diesel exhausts is being carried out by the U.S. Environmental Protection Agency; some preliminary information has already been published.

Since the formation of combustion particles is a primary function of combustion conditions, the potencies of the particles cannot be related simply to the fuel source.

CONCLUSIONS AND RECOMMENDATIONS

The mutagenicity and carcinogenicity of coal, shale, and petroleum crudes tested to date can be ranked in that order, with coal at the top of the scale. Although raw shale liquids fall between coal liquids and petroleum in this list, their activity is closer to that of petroleum.

The differences between the mutagenicities of synthetic and petroleum crudes may be explained by the presence in the former of highly mutagenic alkaline constituents (the polycyclic aromatic primary amines).

---

[a]Common sources of PNH: gasoline and diesel engines, steam plants, power plants, coke ovens, the burning of refuse, and the decomposition of or-

mutagenic and carcinogenic activities of the liquids. The mutagenic carcinogenic activities of hydrotreated shale liquids, for example, differ little from those of petroleum crudes (Cowser, 1980).

Since the hydrocarbons of coal and shale liquids tend to have r complex structures and higher molecular weights than petroleum crude the correlation between boiling point and carcinogenicity in petrole crudes may not be directly applicable to coal and shale liquids. Th is an area that requires study (already underway on Paraho shale oil Additional information is also needed on the toxicity of the highly volatile compounds produced from coal and shale liquids.

Biological testing should be carried out as part of the effort develop a synthetic fuels industry, to determine the nature and exte of the potential risks to the health of workers in such an industry and of the general population.

Since toxicity may be a feature of a particular resource or a t tion of the mode of processing, or both, every aspect requires atte

It would be prudent to have the biological data in hand before making a major investment in production facilities. This calls for integrated effort by fuel technologists and toxicologists on every s of the production process, from the extraction of the resource to th of the final product.

While it is recommended that classical toxicological techniques used to provide definitive information, attention should also be gi new techniques (e.g., bacterial mutagenic tests) that appear useful

BIBLIOGRAPHY

American National Standards Institute. 1969. Acceptable Concentra of Benzene. New York: American National Standards Institute.

American National Standards Institute. 1975. Threshold Limit Valu (TLVs) for Chemical Substances and Physical Agents in the Workroo Environment With Intended Changes for 1975. New York: American National Standards Institute.

Ames, B. N., F. D. Lee, and W. E. Durston. 1973. An Improved Bact Test System for the Detection and Classification of Mutagens and Carcinogens. Proceedings of the National Archives of Science 70: 786.

Ames, B. N., J. McCann, and E. Yamasaki. 1975. Methods for Detect

ntermediates and Products in Oil Shale Operations." Rocky Flats, Colo: he Oil Shale Corporation, Rocky Flats Research Center.

teye, R. 1966. Bladder Carcinogens Occurring During the Production f Town Gas by Coal Carbonization. Hygiene and Toxicology of Occupaional Diseases, International Congress of Occupational Health (Vienna cademy of Medicine) 15(3):153-158.

, R. W., G. Erskine, R. B. Shaller, R. W. Spewak, A. Wallo, and W. L. heaton. 1974. Coke Oven Charging Emissions Control Test Program. cLean, Va.: The Mitre Corporation (M74-45).

enblum, I., and R. Schoental. 1943. Carcinogenic Constituents of hale Oil. British Journal of Experimental Pathology 24:232-239.

rsteker, K., and J. E. Evendijk. 1976. Ozone, Temperature, and Morality in Rotterdam in the Summers of 1974 and 1975. Environmental esearch 12:214-217.

mingham, D. J. 1955. Interim Report on the Shale Oil Study: U.S. ublic Health Service. Cincinnati: U.S. Department of Health, Educaion, and Welfare.

nova, E., I. Veldre, and H. Janes. 1974. Toxicology of Shale Oil and henols. Tallinn, Estonia: Valgus.

t, W. J., L. A. Brinton, J. F. Fraumeni, Jr., and B. J. Stone. 1977. ancer Mortality in U.S. Counties with Petroleum Industries. Science 98:51-53.

ovski, P. A., and H. I. Mirme. 1979. Co-carcinogenicity of Phenols rom Estonian Shale Tars (Oils). Environmental Health Perspectives 0(June):177-178.

ovski, P. A., and F. Vinkmann. 1979. Carcinogenicity of Oil Shale ars, Some of Their Components and Commercial Products. Environmental ealth Perspectives 30(June):165-169.

usgaard, A. 1959. Opptreden av Visse Kreftformer Blant Gassverkareider. [Incidence of Certain Forms of Cancer in Gas Workers.] T. orske Laegeforen 79(12):755-756.

eron Engineers, Inc. 1978a. 1. Endangered Species Found on Oxy's D-a hale Site. 2. Toxic Substances Control Act May Impact Shale Industry. ynthetic Fuels 15(2)(June):2-4. Denver, Colo: Cameron Engineers.

_____. 1978b. 1. Shale Oil Carcinogenicity Demonstrated to Present No Unusual Risks. 2. Union Oil Reviews Projects Revegetation Studies. Synthetic Fuels 15(4)(December):2-31. Denver, Colo.: Cameron Engineers.

_____. 1978c. 1. Shale Oil is Reported for Toxic Substances Control Act. 2. Union, Colony, and Paraho Apply for PSD Permit. 3. EPA Reports Results of Spent Shale Revegetation Study. Synthetic Fuels (15)(3)(September):2-26. Denver, Colo.: Cameron Engineers.

Coffin, D. L. 1980. A Methodological Approach to the Evaluation of the Health Effects of Oil Shale Development. Proceedings 4th US/USSR Joint Symposium of Comprehensive Analysis of the Environment. Washington, D.C.: U.S. Environmental Protection Agency (in press).

Coffin, D.L., M. R. Guerin, and W. H. Griest. 1979. The Interagency Program in Health Effects of Synthetic Fossil Fuels Technologies: Operation of a Materials Repository. Proceedings of the Symposium on Potential Health and Environmental Effects of Synthetic Fossil Fuel Technologies, pp. 153-155. Springfield, Va.: National Technical Information Service (CONF-780903).

Cook, J. W., C. L. Hewett, and S. Hieger. 1933. The Isolation of a Cancer-Producing Hydrocarbon from Coal Tar. Journal of the Chemical Society, Monograph, pp. 395-405.

Coomes, R. M. 1976. Health Effects of Oil Shale Processing. Proceedings of the 9th Oil Shale Symposium. Quarterly of the Colorado School of Mines 71(4):101-123.

Cowser, K. E. 1980. Coal Liquids Evaluation and Paraho-Sohio Shale Oil. Quarterly Progress Report for the Period Ending December 31, 1979. Preliminary Report. Oak Ridge, Tenn.: Oak Ridge National Laboratories (ORNL/TM-7271).

Davis, B. F. 1914. Paraffin Cancer: Coal and Petroleum Products as Causes of Chronic Irritation and Cancer. Journal of American Medical Association 12:1716-1720.

Dietz, W. A., W. H. King, P. W. Priestly, and F. J. Rehner. 1952. Properties of High Boiling Point Petroleum Products. Industrial and Engineering Chemistry, Carcinogenic Studies 44:1818-1827.

Doll, R., R. E. W. Fisher, E. J. Gammon, W. Gunn, G. O. Hughes, S. H. Tyrer, and W. Wilson. 1965. Mortality of Gas Workers with Special Reference to Cancers of the Lung and Bladder. British Journal of Industrial Medicine 22:1-12.

Epler, J. L., and A. W. Hsie. 1978. Genetic Toxicology, Appendix A. Oak Ridge, Tenn.: Oak Ridge National Laboratory (ORNL-5735).

Epler, J. L., F. W. Larimer, C. E. Nix, T. Ho, and T. K. Rao. 1977. Comparative Mutagenesis of Test Materials from the Synthetic Fuel Technologies. In Progress in Genetic Technology, ed. D. Scott, B. A. Bridges, and F. H. Sobels, pp. 275-284. Amsterdam, Holland: Elsevier/North Holland Biomedical Press.

Forney, A. J., W. P. Haynes, S. J. Gasior, G. E. Johnson, and J. P. Strake, Jr. 1974. Analyses of Tars, Chars, Gases, and Water Found in Effluents from the Synthane Process. Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, pp. 107-113. Washington, D.C.: U.S. Environmental Protection Agency (EPA-650/2-74-118).

Gerarde, H. W. 1960. Toxicology and Biochemistry of Aromatic Hydrocarbons. New York: Elsevier Publishing Co.

Guerin, M. R., B. R. Clark, C. H. Ho, J. L. Epler, and T. K. Rao. 1979. Short-Term Bioassay of Complex Organic Mixtures: Part I, Chemistry. In Application of Short-Term Bioassays in the Fractionation and Analysis of Complex Environmental Mixtures, ed. M. D. Water, S. Nesnow, J. L. Huisingh, S. S. Sandhu, and L. Claxton. Environmental Science Research Series, Vol. 15, pp. 247-268. New York: Plenum Press.

Guerin, M. R., C. H. Ho, T. K. Rao, B. R. Clark, and J. L. Epler. 1980. Polycyclic Aromatic Amines as Determinant Chemical Mutagens in Petroleum Substitutes. Environmental Research 23(1)(October):(in press).

Heiger, I., and D. L. Woodhouse. 1952. The Value of the Rabbit for Carcinogenicity Tests on Petroleum Fractions. British Journal of Cancer 6:293-299.

Heller, I. 1930. Occupational Cancer. Journal of Industrial Hygiene 12:169-197.

Henry, S. A. 1937. The Study of Fatal Cases of Cancer of the Scrotum from 1911 to 1935 in Relation to Occupation with Special Reference to Chimney Sweeping and Cotton Mule Spinning. American Journal of Cancer 31:28-57.

_____. 1947. Occupational Cutaneous Cancer Attributable to Certain Chemicals in Industry. British Medical Journal 4:389-401.

Distillates. Washington, D.C.: U.S. Department of Energy.

Holt, J. P., N. V. Hendricks, R. E. Eckhardt, C. L. Stanton, and R. C. Page. 1951. Symposium: A Cancer-Control Program for High-Boiling Catalytically-Cracked Oils. Archives of Industrial Hygiene and Occupational Medicine 4:297-345.

Horton, A. S., E. L. Bingham, M. J. Graf Burton, and R. Tye. 1965. Carcinogenesis of the Skin: 3. The Contribution of Elemental Sulfur and of Organic Sulfur Compounds. Cancer Research 25(10):1759-1763.

Hueper, W. C. 1942. Occupational Tumors and Allied Diseases. Springfield, Ill.: Charles C. Thomas.

_____. 1956a. Experimental Carcinogenic Studies on Hydrogenated Coal Oil. Industrial Medicine and Surgery 25:51-55.

_____. 1956b. Experimental Studies of Carcinogenesis of Liquid Fuels and Petroleum Substitutes. Industrial Hygiene and Occupational Medicine. Chicago: American Medical Association.

Jones, A. R., M. R. Guerin, and B. R. Clark. 1977. Preparative-Scale Liquid Chromatographic Fractionation of Crude Oils Derived from Coal and Shale. Analytical Chemistry 49(12):1766-1771.

Kaden, D. A., R. A. Hites, and W. G. Thilly. 1979. Mutagenicity of Soot and Polycyclic Aromatic Hydrocarbons to Salmonella typhimurium. Department of Nutrition and Food Science. Massachusetts Institute of Technology. Cancer Research 39(10):4152-4159.

Kennaway, E. L. 1924a. On the Cancer-Producing Factor in Tar. British Medical Journal 1:564-566.

_____. 1924b. On Cancer-Producing Tars and Tar Fractions. Journal of Industrial Hygiene 5(12):462-466.

_____. 1925. The Anatomical Distribution of Occupational Cancers. Journal of Industrial Hygiene 7:69-73.

Kennaway, E. L., and I. Hieger. 1930. Carcinogenic Substances and Their Fluorescence Spectra. British Medical Journal 1:1044-1046.

Ketcham, N. H., and B. S. Norton. 1960. The Hazards to Health in the Hydrogenation of Coal: 3. The Industrial Hygiene Studies. Archives of Environmental Health 1:194-207.

King, P. J. 1969. The Carcinogenic Action of Mineral Oils. Industrial

ities of the Institute of Experimental and Clinical Medicine, pp. 22-30. Tallinn, Estonia. (In Russian.)

Laster, L. I. 1973. Atmospheric Emissions from the Petroleum Refining Industry. Washington, D.C.: U.S. Environmental Protection Agency (EPA-650/2-73-017).

Lawther, P. J., B. T. Cummins, and R. E. Waller. 1965. A Study of the Concentrations of Polycyclic Aromatic Hydrocarbons in Gas Workers Retort Houses. British Journal of Industrial Medicine 22:13-20.

Legge, T. M. 1911. Special Report on Ulceration of the Skin and Epitheliomatous Cancer. London: H.M. Stationery Office.

_____. 1922a. Epitheliomatous Ulceration. Annual Report, Chief Inspector for Factories and Workshops for 1921, p. 78. London: H.M. Stationery Office.

_____. 1922b. Epitheliomatous Ulceration in Industry. British Medical Journal 2:1110.

Leitch, A. 1922. Paraffin Cancer and Its Experimental Production. British Medical Journal 2:1104-1106.

Lowry, H. H., ed. 1963. Chemistry of Coal Utilization. New York: John Wiley & Sons.

McMichael, A. J., R. Spiritos, L. L. Kupper, and J. F. Gamble. 1975. Solvent Exposure and Leukemia among Rubber Workers. Journal of Occupational Medicine 17:234-239.

National Research Council. 1977. Assessment of Technology for Liquefaction of Coal. Ad Hoc Panel on Liquefaction of Coal, Committee on Processing and Utilization of Fossil Fuels, Commission on Sociotechnical Systems. Washington, D.C.: National Academy of Sciences.

Parkinson, G. S. 1971. Benzene in Motor Gasoline: An Investigation Into Possible Health Hazards In and Around Filling Stations and in Normal Transport Operations. Annals of Occupational Hygiene 14:145-153.

Pelroy, R. A., J. T. Cresto, and M. R. Petersen. 1979. Mutagenicity of Shale Oil and Solid Refined Coal Fractions. Pacific Northwest Laboratory Annual Report/Biomedical, pp. 5.5-5.9. Richland, Wash.: Pacific Northwest Laboratory.

Pelroy, R. A., and M. R. Petersen. 1979. Use of Ames Test in Evaluation of Shale Oil Fractions. Environmental Health Perspectives 30(June):

Pott, P. 1775. Chirurgical Works. Vol. 5, p. 63. London: Wood & Innes.

Prev, M., ed. 1945. High Pressure Hydrogenation at Ludwigshafen, Heidelberg. 8 vols. I. G. Farben Industrie.

Purde, M., and M. Rahu. 1979. Cancer Patterns in the Oil Shale Area of the Estonian S.S.R. Environmental Health Perspectives 30(June):209-210.

Redmond, C. K., A. Ciocco, J. W. Lloyd, and H. W. Rush. 1972. Long-Term Mortality Study of Steel Workers. 6. Mortality from Malignant Neoplasms Among Coke Oven Workers. Journal of Occupational Medicine 14(8):621-629.

Rubin, I. B., M. R. Guerin, A. A. Hardigree, and J. L. Epler. 1976. Fractionation of Synthetic Crude Oils from Coal for Biological Testing. Environmental Research 12:358-365.

Rushton, L., and M. R. Alderson. 1980. An Epidemiological Survey of Eight Oil Refineries in the U.K.--Final Report. London: Institute of Petroleum.

Sauter, D. Y. 1975. Synthetic Fuels and Cancer. New York: Scientists Institute for Public Information.

Schuchardt, K. 1885. Beitrage zur Entstehung der Carcinome aus Cronisch Entzundliches Zustanden der Schleimhaute und Hautdecker. Sammlung Klinischer Vortrage (Leipzig) 257(80):2195-2238.

Schwartz, L. 1934. Dermatoses Caused by Petroleum. Occupational Diseases of the Skin (2nd edition), ch. 14. London: Kimpton.

Scott, A. 1922. On the Occupation Cancer of the Paraffin and Oil Workers of the Scottish Shale Oil Industry. British Medical Journal 2:1108.

Sexton, R. J. 1960. The Hazards to Health in the Hydrogenation of Coal: 1. Introduction Statement and General Information; 4. The Control Program and the Clinical Effects. Archives of Environmental Health 1:181-186, 208-230.

Sherwood, R. J. 1972. Evaluation of Exposure to Benzene Vapor During Loading of Petrol. British Journal of Industrial Medicine 29:65-69.

Shopek, T. R., H. L. Liber, J. J. Krolewski, and W. G. Thilly. 1978a. Quantitative Forward Mutation Assay in Salmonella typhimurium Using 8-Azaguamine Resistance as a Genetic Marker. Proceedings of National Academy of Sciences 75:410-414.

. 1978b. Relative Sensitivity of Forward and Reverse Muta-

Smith, W. E., D. A. Sunderland, and K. Suguira. 1951. Experimental Analysis of the Carcinogenic Activity of Certain Petroleum Products. Archives of Industrial Hygiene and Occupational Medicine 4:299-314.

Tabershaw/Cooper Associates. 1974. A Mortality Study of Petroleum Refinery Workers Project OH-1. Medical Research Report #EA 7402. Washington, D.C.: American Petroleum Institute.

_____. 1975. A Mortality Study of Petroleum Refinery Workers: Social Security Follow-up. Project OH-1, no. 129. Washington, D.C.: American Petroleum Institute.

Thorpe, J. J. 1974. Epidemiologic Survey of Leukemia in Persons Potentially Exposed to Benzene. Journal of Occupational Medicine 16:365-382.

Tillmanns, H. 1880. Ueber Theer-, Russ- und Tabakkrebs. Deutsche Zeitschrift fur Chirurgie 13:519-535.

Treibl, H. G. 1967. Naphthalene Derivatives. Encyclopedia of Chemical Technology, 2nd edition. New York: John Wiley and Sons.

Tsuitsui, H. 1918. Uber das Kunstlich Erzeugte Cancroid bei der Maus. Gann 12:17-21.

Twort, C. C., and J. M. Twort. 1931. The Carcinogenic Potency of Mineral Oils. Journal of Industrial Hygiene and Toxicology 13:204-226.

U.K. Medical Research Council. 1968. The Carcinogenic Action of Mineral Oils: A Chemical and Biological Study. Special Report Series No. 306. London: H.M. Stationery Office.

U.S. Department of the Interior. 1968. Hydrogenation of Coal and Tar. Bureau of Mines Bulletin 633. Washington, D.C.: U.S. Department of the Interior.

_____. 1975. Mineral Facts and Problems. Bureau of Mines Bulletin 667, pp. 963-988. Washington, D.C.: U.S. Department of the Interior.

Veldre, I. A., and H. J. Janes. 1979. Toxicological Studies of Shale Oils, Some of Their Components and Commercial Products. Environmental Health Perspectives 30(June):141-146.

von Volkmann, R. 1875. Uber Teer-, Paraffin- und Dustkrebs (Schornsteinfegerkrebs). Beitrage zur Chirurgie (Leipzig), p. 370.

of Mice. Archives of Environmental Health 1:187-193.

White, R. P. 1926. Modern Views on Some Aspects of the Occupational Dermatoses. Journal of Industrial Hygiene 8(9):367-381.

Yamagawa, K., and K. Ichikawa. 1915. Experimentelle Stude uber die Pathogenese der Epithelialgeschwulste. Mitteilungen der Medizinischen Facultat der Kaiserlichen Universitat zu Tokio 15:295-344.

10 RESEARCH AND DEVELOPMENT

Federal funding of research and development should focus on activities that augment but do not duplicate the R&D that private industry can carry on effectively.

Federal support is appropriate for (a) high-priority projects whose costs or risks limit support by private enterprise, (b) long-term development programs with distant payoffs, and (c) programs that, for strategic reasons, are needed to develop technologies earlier than they would be developed if left to market forces. Another responsibility of the government is research and development directed specifically at protecting the environment and the health and safety of the public and the work force.

Synthetic fuels can, at present, be refined with known or partly developed processes based on privately developed petroleum refining technology. The necessary research and development, in the judgment of industrial experts, is low in both cost and financial risk and is a direct extension of ongoing research programs devoted primarily to petroleum refining. Given reasonable expectations of a market in the relatively near future, the private sector can provide the necessary refining technology without federal R&D funds. Many private concerns, in fact, are reluctant to seek federal support, which, in their views tends to stifle incentives for industry to spend its own funds on R&D, threatening the traditional competitive conduct of proprietary research and development.

The Department of Energy has a responsibility for ensuring that the necessary technology will be available when needed, however, and some participation in refining R&D appears necessary so that advanced technol-

refining of hydrocarbon liquids for use as burner and transportation fuels. In addition, current projects sponsored by the Department of Energy were reviewed informally with members of the Department and their contractors.

FEDERALLY FUNDED R&D

The Department of Energy sponsors a limited amount of basic and exploratory research in fields pertinent to synthetic liquid refining and the indirect liquefaction of coal. At one point, the government planned a 100-barrel-per-day plant to test refining processes and produce products for evaluation but this was dropped because of budget limitations.

The basic and exploratory work sponsored by the Department of Energy is done by universities, federal laboratories, and industrial concerns, with pilot-scale projects handled by contract with industry. A number of universities are investigating the chemical, physical, and thermal properties of various coal-derived liquids, and the Bartlesville, Laramie, and Pittsburgh Energy Technology Centers are carrying on similar work with coal and shale liquids. Federally sponsored programs at universities, federal Energy Technology Centers, and at least one private R&D firm are studying the chemistry of catalytic refining.

Also being carried on at government laboratories are limited attempts to apply modern petroleum refining practices to synthetic crudes; the projects are mainly bench-scale experiments with variations in catalysts and process conditions. Some universities are also experimenting with process and catalyst variations.

Chevron Research Co. began conducting bench-scale refining tests of shale oil and coal liquids in 1977 with Department of Energy support, using conventional refining techniques. This effort is currently focusing on cutting costs. Universal Oil Products is conducting similar contract work.

The Navy contracted early in fiscal year 1977 for 60,000 to 100,000 barrels of shale oil from the Anvil Points Facility, operated jointly by industry and the Department of Energy. This oil is being refined to military product specifications so that full-scale tests of the resulting products can be conducted. The Air Force is also funding research and development work to determine the most cost-effective way of refining whole shale oil to low-nitrogen turbine fuel.

The canceled pilot-scale plant, planned by the Department of Energy, to produce transportation fuels from coal liquids will still be needed to produce fuels for full-scale testing in currently available engines. It

work in refining R&D.[a] Bartlesville has a unique thermodynamics laboratory and an engine-testing facility where, using a total systems approach, studies are being made of optimal combinations of refining facilities and engine types. Laramie is field testing *in situ* coal gasification processes and is also monitoring all of the DOE's shale contracts. Pittsburgh, the largest of the three centers, remains a leader in the conversion of coal to liquids and gases.

The analytical capabilities are excellent at all three centers, particularly at Bartlesville, where the equipment includes the latest in facilities of this type. The extensive analyses of liquids being obtained at all three locations will prove very helpful in guiding research and development in this area. Laramie concentrates on shale oils and Pittsburgh on coal liquids, with Bartlesville working on both. Laramie is the only center that has done a significant amount of work in refining, having made studies of coking, hydrotreating, and hydrocracking of shale oils for more than 20 years. However, the equipment at Laramie is old and limited in scope, and appears inadequate for the type of experimentation that will be needed in this area. Pittsburgh, on the other hand, has just installed modern continuous units for refining coal liquids; these units are being tested.

One of Bartlesville's major functions is monitoring contracts on enhanced oil and gas recovery. This center, with a staff of about 190, has a long background of cooperative work with the petroleum industry, including projects (sponsored by the American Petroleum Institute) in characterizing crude oils and individual compounds in petroleum. Efforts on refining have been limited to paper studies of the application of existing petroleum processes, but a small multipurpose hydrogenation unit installed recently will give the laboratory some "hands-on" experience in refining. Bartlesville's thermodynamics laboratory and engine test facilities have been used on a cooperative basis to carry out work for other government departments and for industry.

Laramie, in addition to monitoring oil shale contracts, is carrying out in-house work on shale oil composition and *in situ* retorting. Its work on one of the fractions of shale oil, a very heavy tar, includes the characterization of this material and an evaluation of its use as asphalt for road construction. The annual reports that have been issued are

---

[a]The National Laboratories (Oak Ridge, Argonne, Brookhaven, Sandia, and Lawrence Livermore) and the other Technology Centers (for example, Morgantown and Grand Forks) also have considerable capacity for research and development in the refining of synthetic fuels.

The Pittsburgh Energy Technology Center at Bruceton, Pennsylvania, with a staff of 470, is part of a complex which also includes facilities of the Department of Labor's Mining Safety and Health Administration and the Department of the Interior's Bureau of Mines. Other Department of Energy functions at that location include the 75-ton-per-day Synthane pilot plant, the 10-ton-per day Liquefaction Test Facility (formerly the Synthoil PDU), and the Pittsburgh Mining Operations Center, which is carrying out research in longwall and conventional mining. Until the summer of 1978, work on the refining of coal liquids at Pittsburgh had been limited to batch autoclave experiments, the results of which were difficult to translate into conclusions about large-scale continuous operation. Pittsburgh has since expanded its laboratory facilities and now has two flow-type hydrogenation units, instrumented to give a complete set of data. Its capability for catalyst and other process research has also been expanded.

In considering the general problem of research on the refining of coal and shale liquids, this panel concludes that major research and development on processes should be handled by industry, not only because they will be the ultimate users of the technology but also because they have built excellent facilities and have trained personnel to carry out the work. It is recommended that the Energy Technology Centers keep work of this type to the minimum level necessary to maintain familiarity with the field. This panel also concludes that long-range basic research on the refining of these liquids should be sponsored by the government; while a substantial amount of relevant basic and exploratory work being carried out by industry, government support can have the desirable effect of accelerating progress in the development of new processes.

In view of the relatively limited manpower and facilities available at Bartlesville and Laramie, it appears that neither is in a position to carry out in-house, longer range research. But Laramie can monitor development-type contracts on the refining of shale oils, drawing heavily on its staff's knowledge of the constitutions of these materials, and Bartlesville can do the same for coal liquids, based on its staff's analytical knowledge and their familiarity with petroleum processing techniques.

The center at Pittsburgh, where a Process Sciences Division has been set up with a Catalysis Branch, a Process Development Branch, and a Chemistry Branch, is in the best position to carry out some limited work in-house and to monitor contract work with universities, industry, and nonprofit institutions.

Thus, while the Energy Technology Centers do not have the resources

nel conducted an informal poll of 37 private concerns, including ect-engineers, petroleum refiners, and catalyst manufacturers, that w conducting refining research and development and might be expected tinue developing technology for refining coal and shale liquids. uld be stressed that this was not a comprehensive survey. It was ed only to provide general information about efforts by private ry in this field. The questionnaire used is included as an appendix s chapter.

Twenty-nine companies responded. The detailed responses must be kept dential, but the aggregated statistics give a general picture of the s being made and of industry views on where (or if) federal funding e effectively spent on these problems.

The results reveal that perhaps 2000 people, professional and non-ssional, are working in private industry on all forms of refining rch. Ten to twenty percent of the effort is devoted specifically e refining of coal and shale liquids, including basic research and -scale and pilot-plant work. Approximately half the effort specifi- devoted to synthetic fuel refining is funded by the federal govern- The 29 responding companies have, in all, devoted more than 1000 n-years to coal and shale liquid refining problems.

Fifteen companies answered the question whether basic exploratory rch in these subjects is needed, all of them in the affirmative. added that government and industry should sponsor such work jointly, wo stated that industry alone should be involved. Ten respondents red the question whether development and demonstration work is d, all in the affirmative; five recommended joint government-industry orship, and two expressed the belief that industry itself should e sole source of funds.

In their general comments, four companies favored government involve- in defining needed areas of research and coordinating the R&D effort. were opposed to government intervention, stating that refining re- h is low in both risk and cost, that the petroleum industry will op the necessary technology, and that government funding in the etic liquid fuel field should be aimed at liquefaction processes r than refining.

Most of the responding companies, in answer to a question about re- h needs, recommended that research be carried out on the following:

- Longer lived catalysts

- Low-cost methods for producing hydrogen
- Inexpensive and effective means of removing nitrogen and sulfur from the products
- Improvements in product stability, to allow longer storage
- The chemistry of raw liquids and their chemical behavior during processing
- The economically optimum combination of various final products and end-use devices.

The panel is familiar with industrial research and development in this field, and has been able to identify strong and weak points. The major problem is not a technical one, but rather the uncertainty about economic factors. No one is certain when commercialization will occur, and there is consequently no incentive for a high-priority full-scale commitment by industry.

At present, most research and development in this area is carried out under government support, with cost-sharing by industry. Experimental work in the industrial laboratories is being done primarily on the following:

- The development of more selective catalysts for nitrogen and sulfur
- The development of catalysts with longer life
- The investigation of operating parameters affecting the upgrading of solvent refined coal via expanded bed catalytic hydrogenation
- Catalytic cracking and hydrocracking of hydrogenated coal-derived and shale-derived gas oils
- The removal of ash from coal-derived liquids without the use of filters or centrifuges.

In carrying out this work, industry is drawing on its accumulated experience and expertise in petroleum refining.

The scope and level of industrial activity appear sufficient to yield practical technologies for converting coal to liquid fuels, but a strong effort to optimize these technologies cannot be expected until the economics are favorable. The case of shale oil is somewhat different.

right. These firms believe that the time required for final pilot-plant studies, optimization and construction will be available during the time period between a decision to produce shale oil commercially and the need for production quantities.

R&D PRIORITIES

The informal and selective survey of R&D work in progress, and the experience of the members of this panel, permits identification of the most important fields for R&D in synthetic liquid fuels refining. They are summarized here; more detailed technical discussions appear elsewhere in this report.

Future Product Requirements

Liquids produced directly from coal and shale are considerably more costly to refine to meet current gasoline and distillate fuel specifications than is petroleum. The highest boiling fractions of coal liquids are expected to be used initially in applications where little refining is necessary, as in power plants and large industrial boilers. Fractions boiling in the same temperature range as gasoline will likely be used to produce gasoline because of their high octane numbers. But the use of coal liquids for the production of distillate fuels is expected to be delayed. Shale liquids, with their higher hydrogen contents, will be more attractive for the production of high-quality transportation fuels.

By the time synthetic fuels are produced in any quantity, the relative demand for various liquid fuels will probably have changed. Gasoline, for example, is expected to constitute a smaller proportion of total hydrocarbon demand in the future than it does today, while mid-distillate fuels of high hydrogen content (diesel and jet fuels, home heating oil, and the like) will grow in importance. This is something of a problem in view of the low hydrogen contents of coal liquids and the high cost of hydrogenation. Now under study are combustion equipment designs that can use fuels with lower hydrogen contents (e.g., gas turbines, stratified-charge engines, and Stirling-cycle engines), but they are not likely to be used on any significant scale before the turn of the century.

At present, engine manufacturers and fuel refiners are looking to each other for direction. The need for collaboration is recognized, but any shift in products and fuels will be slow in coming. Practical engine-fuel systems require considerable effort, not only on the technical and engineering problems but also on the financial and institutional arrangements that will be needed to optimize costs and efficiencies.

liquids that have heavier burdens of nitrogen, sulfur, and various trace elements. As these impurities tend to deactivate conventional catalysts, it is vital to understand the deactivation mechanisms.

Especially important is the need for selective hydrodenitrogenation catalysts. Since nitrogen degrades product stability and pollutes the air when the products are burned, it must be removed from fuels that are to be used in many end-use devices. Unfortunately, available catalysts tend to saturate the raw liquids with hydrogen before removing nitrogen, resulting in high hydrogen consumption. Hydrodenitrogenation catalysts that are as selective as available hydrodesulfurization catalysts need to be developed. Federal support of basic research relevant to this problem is recommended.

Shale oils present a particular problem because their arsenic contents are generally high. Arsenic is highly toxic and, in addition, rapidly deactivates refining catalysts. Industry is already attacking this problem, but long-range studies of arsenic's chemical forms in shale oil, its specific catalyst deactivation mechanisms, and its removal would be helpful.

Disposal of Arsenic Wastes from Shale Oil Refining

Traces of arsenic remain in spent shale and enriched deposits of arsenic accumulate in spent guard chamber clays and hydrofining catalysts (probably as As_2S_3) during shale oil refining; these must be disposed of in an environmentally acceptable manner. As_2S_3 is reported to be pyrophoric; hence, a controlled incineration is probably required. Since impervious clay deposits are frequently found in underlying shale deposits, the disposition of oxidized spent clays and catalysts in compacted spent shale is a reasonable possibility. Evaluation and pilot testing of this procedure is needed.

An alternative, more expensive procedure is disposition through long term storage procedures at a national disposal site (U.S. Environmental Protection Agency, 1973).

Hydrogen Production

Because coal liquids are relatively low in hydrogen content, large amounts of hydrogen must be added during the refining process to produce high-quality hydrocarbon fuels. Hydrogen is also needed to remove the sulfur and nitrogen. All commercial methods of hydrogen production are costly and contribute heavily to the costs of the ultimate products. While some possibilities exist for reducing the cost of producing hydro-

if a promising possibility developed, a sharing of R&D costs between DOE and industry would be desirable. Exploratory and basic work on new approaches to hydrogen production should be supported by the Department of Energy where good ideas and competent research teams can be identified.

Chemistry of Raw Liquids and Chemical Reactions in Refining

The chemical properties of shale liquids differ markedly from those of petroleum. They are, in general, more heavily laden with nitrogen, sulfur, and oxygen, and some contain wide varieties of trace elements. Coal liquids from direct conversion processes contain large concentrations of polycyclic aromatic compounds, a few of which are known carcinogens.

These characteristics have important implications for refining, the environment, and the health of synthetic fuel workers and the public. A comprehensive and accurate picture of the compositions of coal and shale liquids is obviously vital. While some federally funded work is being carried out at universities and federal laboratories, more effort is needed in these areas.

Indirect Liquefaction

Indirect coal liquefaction may prove competitive with direct liquefaction as a means of producing gasoline, diesel fuel, and jet fuels. The indirect process (involving gasification, gas purification, and subsequent liquefaction) has the advantage of removing all of the impurities of the feed coal but, in the Fischer-Tropsch process as operated commercially at SASOL, it results in an olefinic gasoline that requires further treatment. In addition, the SASOL gasoline contains a range of chemicals that must be separated out for other applications or further conversion.

If more selective catalysts for indirect liquefaction can be developed, this Fischer-Tropsch process, which now appears to be more expensive than direct liquefaction, will appear more competitive when the overall goal is considered. Research on new catalysts, with the objective of producing a greater proportion of transportation fuel of the desired quality should be encouraged. Some very promising developments have taken place recently; for example, industry has developed an indirect process for the selective conversion of synthetic gas to high-octane gasoline by converting the gas to methanol, which is then converted to high-octane gasoline over a zeolite catalyst.

Health and Environmental Impacts

impacts on ecological systems and the health of workers and the general public must be established with greater precision than is now possible. Finally, suitably effective control technologies must be made available.

In the human health field, the first task is to identify the populations most at risk, by means of multimedia exposure assessments that take into account all sources of exposure; presumably the most heavily exposed population will be that of workers in refineries, and those who must handle certain refined products. Complex mixtures of substances will be involved, and their possible interactions must be accounted for. Workers should be monitored for signs of exposure-related health problems, and a follow-up registry should be maintained so that their conditions may be checked periodically in the future. Clinical and laboratory studies of the metabolism of toxic, carcinogenic, co-carcinogenic, and mutagenic materials should be made to identify the main risks and useful indicators of exposure.

Studies of the ecological effects of refinery effluents and emissions should begin with accurate assessments of the compositions and release rates of all wastewaters, solid wastes, and emissions to the atmosphere. Site-specific studies of pollutant effects and pathways in the environment should begin early enough so that later recognition of the need for tighter control does not impose undue retrofit requirements on refining systems, and control technologies should be assessed in terms of their effectiveness in controlling all pollutants of concern.

RECOMMENDATIONS

Although refining processes capable of producing conventional fuels from oil and shale are available, high hydrogen consumption, poor selectivity, and, in some cases, low catalyst activity and life indicate the need for major improvements. The petroleum industry in the United States is capable of developing synthetic fuel refining processes and is carrying on a considerable amount of exploratory research, but the clearly distant need for major synthetic fuel refining facilities has delayed a major effort at commercialization. As complements to the research and development efforts of the petroleum industry, the panel recommends that the government support its own program, emphasizing basic and exploratory research.

Basic and Exploratory Research

- Reaction mechanisms for the selective removal of nitrogen, as a means of reducing the consumption of hydrogen

- The deactivation mechanisms of selective catalysts for the removal of nitrogen, oxygen, and arsenic

- New catalytic materials.

llowing problems should be given moderate priority:

- The forms in which arsenic is present in shale oil, and reaction mechanisms for its removal

- The mechanisms of the viscosity and solubility changes that occur during the storage of some coal liquids

- The factors that determine selectivity in indirect liquefaction.

roblems in the following list deserve relatively low priority in al research and development:

- Reaction mechanisms for the removal of oxygen from synthetic liquids

- The deactivation mechanisms of desulfurization catalysts.

Applied Research and Process Development

industry is able and willing to develop refining technology to modate synthetic liquids, the federal government should monitor ess and maintain enough expertise to allow efficient regulation dentification of emerging basic research problems. This will l the funding of some small applied research projects in the y Technology Centers, universities, and industry.

In such a program, methods of selective nitrogen removal and tech- s for lowering the cost of hydrogen, and synthetic gas, and the opment of longer lived catalysts for removing nitrogen, oxygen, rsenic deserve the highest priority; all could strongly reduce ction costs. On the next order of priority are methods of selec- arsenic removal, more selective catalysts for indirect liquefaction, dditives to improve the stability of coal and shale liquids. A priority should be given to methods of selective oxygen removal evelopment of longer lived catalysts for desulfurization.

Because the economics of synthetic fuels depend heavily on the extent to which they must be upgraded for use in engines and burners, it would be useful to optimize fuels and end-use equipment, considered as a system. The development of engines and burners that can use less refined fuels, for example, might pay large returns in overall efficiency and economy. Large scale engine and burner tests would be required in such a development effort, and suitably large supplies of refined fuels. The facilities, including a small refinery, would be too expensive for any private company to construct, and a government-industry cooperative program might be appropriate.

BIBLIOGRAPHY

U.S. Environmental Protection Agency. 1973. Recommended Method of Reduction, Neutralization, Recovery, or Disposal of Hazardous Waste, Vol. 6. Washington, D.C.: U.S. Environmental Protection Agency (PB-224-585).

PRIVATE CONCERNS INVOLVED IN REFINING R&D

November 22, 1977

irs:

t the request of the Department of Energy (formerly ERDA) the
al Research Council has formed an ad hoc panel to investigate the
ch and development needs related to the refining of synthetic crude
btained from coal and oil shale. The specific objective of the ad
nel is to:

efine the research and development needs in refining coal and shale
iquids to a product slate emphasizing transportation fuels and other
istillable fuels.

er to accomplish this objective, the panel will:

urvey the programs currently underway on processing techniques
pplicable to coal and shale upgrading. Programs are currently
upported by Industry, Department of Energy, Department of Defense
nd the Electric Power Research Institute (EPRI).

ith the results of the above, define the areas in coal and shale
efining and upgrading where research would be desirable from a
enefit to cost standpoint and from the standpoint of national needs.

rrent composition of the panel is attached to this letter.

s indicated in the statement of task, a measure of magnitude and
of R & D programs aimed at advancing the technology of refining
nd shale liquids is needed in order to define research needs in this

t is recognized that a substantial fraction of petroleum refining
logy is applicable to the refining of coal and shale liquids and
etroleum refining research and development capabilities could po-
lly be focused on research dealing with the special characteristics
l and shale liquids such as high nitrogen content, high aromatic
t, high oxygen content, etc. For hydrogen manufacture, programs
at cost reduction where coal or coal char is the starting material
be relevant. Similarly, studies of product composition requirements
focus on the effect of high nitrogen content on fuel stability or

petroleum refining research and development listed above.

For consistency, it is recommended that the information include

1. Total laboratory and staff professional personnel directly engaged in research and development on the refining of hydrocarbon liquids including those from tar sands, shale oil and coal, as well as from crude petroleum.

2. The fraction of this effort specifically devoted to refining of coal and shale liquids. This might include problems related to:

   a) sulfur removal
   b) nitrogen removal
   c) boiling range conversion
   d) hydrogenation
   e) hydrogen manufacture
   f) product composition
   g) fuel stability
   h) others

3. The split between Basic & Exploratory, Bench Scale and Pilot Plant.

4. Fraction of this work supported by government funds.

5. Your comments on research needs in this area.

The industrial information gained in this survey will be presented in aggregated form; thus we will not reveal, in any way, the specific activities of any one company. The information will be listed under the categories of:

- Petroleum companies
- Process research and construction companies

Please let me stress that the data provided will be used only to help the panel complete its objective; that is, providing meaningful recommendations to the Department of Energy on where research and development should be concentrated.

I would appreciate it if we could receive your response by Jan. 2, 1978. Your cooperation in gathering this information will be greatly appreciated.

Sincerely yours,

John O. Berga